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# DEVELOPMENT OF HYDROGENATION CATALYSTS

by

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# FOREWORD

This report presents the results obtained during a study of the "Development of Catalyst for Hydrogenation of Condensed Polynuclear Aromatic Compounds" supported by Energy Mines and Resources under contract number OSQ 80-00199. The study was carried out over twelve months period. Polynuclear aromatic compounds constitue a major fraction of relatively abundant hydrocarbon sources, such as the bitumen of Athabasca Tar Sand, creosote oil and pitch. The uptake of hydrogen by the polynuclear aromatic hydrocarbons is of industrial interest as it leads to the formation of products, which are more liquid and more suitable as fuels in internal conbustion engines. It may take place by the saturation of multiple bonds and by the hydrogenolysis of single bonds between carbon-carbon, carbon-oxygen, carbon-sulfur, and carbon-nitrogen atoms.

The work of this project was confined to phenanthrene, anthracene and naphtahalene which are typical of the hydrocarbons produced during the liquefaction of coal. In this investigation , Flash Hydorpyrolysis (FHP) in the presence of catalyst has been found to be the most useful technique for converting these compounds to desirable products in high yields.

This work is continuing. The objective will be a quantitative determination of liquid and gaseous products formed. An additional objective will be to apply the FHP process for upgrading of bitumen samples.

Any comments and suggestion from users of this report will be most welcome.

R. N. P.

## ABSTRACT

Hydrogenation of phenanthrene, anthracene and naphthalene over sulfided Ni-W and sulfided Co-Mo catalysts was studied over a range of conditions considered to be moderate to severe: temperature, 500 - 700°C, pressure = 1000 psig. The reaction was studied in a Flash Hydrogpyrolysis reactor. In majority of experiments the ratio of catalyst/sample varied from 6 to 8 (wt/wt). The products condensable at - 78°C were analyzed by gas chromatography-mass spectrometry. Thé conversion of phenanthrene and anthracene was about 80% at 500°C. However, naphthalene requires more severe conditions. Forty G.C. peaks were detected with an SE30 capillary column and twenty four products were identified. The conversion to lower molecualr weight species and highly desirable products was the observed result. This preleminary study is therefore of considerable interest as it offers potential for process development and stimulates further detailed study.

## ACKNOWLEDGEMENT

A number of individuals made contributions during the course of this study. Mr. Leo A. Rodrigues helped on the design and assembly of electrical heating system for the Flash Hydropyrolysis Apparatus. Mr. Hans Schroeder provided assistance in the mechanical assembly of the apparatus. Mr. P.K.Dixit, and Mr. F. Haniff, helped Bruce Johnson in carrying out FHP runs. Dr. Ray Clement, research associate, Chemistry Department of the University of Waterloo carried out GC/mass spectral runs. On various occasions the author had helpful discussion with Dr. A. Effio and Dr. G. Kruger. The enthusiastic support of all these individuals are gratefully acknowledged and appreciated.

Numerous problems were encountered in the assembly and operability of FHP apparatus. The author remains indebted to Dr. Marten Ternan of EMR, for his infinite patience and encouragement throughout this investigation.

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| | Unsuccessful experiments for attempted hydrogenation of phenanthrene with formic acid and its salts in the presence of catalysts. | |

# I INTRODUCTION

Upgrading of high molecular weight, residual material is becoming increasingly important as a result of decreasing availability of lighter feedstocks. The processes for conversion must be efficient in the presence of hetroatom content, high aromaticity, high molecular weight (low volatility) not encountered to the same degree in lighter feedstocks. These characteristics result in higher process costs and lower conversion and desired products.

In recent years much interest has been taken in the conversion of coal, oil sand and biomars to gasoline. The conversion of these indeed offer a potential alternative to importing ever increasing amounts of crude petroleum in the near and intermediate future.

In the long term, as world petroleum reserves becomes depleted, a synthetic fuel industry seems certain to develop and prosper. At the present time it appears that the most attractive means of converting coal to gasoline is through the production of a synthetic crude, it is envisioned it would then be processed in a more or less conventional petroleum refinery.

One of the promising techniques for converting hydrocarbon feedstocks such as coal, oil sand and biomass into useful synthetic fuel liquids and gases is the Flash Hydropyrolysis

(FHP) technique. The FHP process has attracted considerable attention because it offers a comparatively simple method of converting coal to commercially valuable products such as Synthetic Natural Gas (SNG), fuel oil, BTX liquids (benzene, toluene, xylenes) (1,2,).

The purpose of the present investigation is to use the FHP technique on the hydrogenolysis of model compounds, such as phenanthrene, anthracene and naphthalene over sulfided Co-Mo and sulfided Ni-W catalysts.

Phenanthrene is typical of the hydrocarbons produced during the liquefaction of coal, with the staggered phenanthrene like compounds being thermodynamically more stable than the linear anthracene like isomers (3). Phenanthrene derivatives are usually present in greater abundance in coal derived liquids (4).

Pure model compounds were Flash hydropyrolysed over the catalysts in a FHP reactor. Analysis of the products was undertaken in order to identify the major products. The data have been carefully examined for conversion. The products indicate the conversion involving splitting at the central ring. The products observed are highly desirable and the conversion is found to be high. In this report our preliminary data on FHP of phenanthrene, anthracene and naphthalene is presented and direction for future work is indicated.

## II THERMODYNAMICS CONSIDERATIONS

An understanding of the thermodynamics of the hydrogenation of phenanthrene will provide an insight in the interpretation of the data obtained in the present study. Thermochemical data on anthracene, naphthalene and phenanthrene is presented in table 1 (5).

Table 1

Thermochemical Data

| Compound | $\Delta H^{\circ}_{f}298^{\circ}$ (K cal/ g mole) | $\Delta G^{\circ}_{f}298$ (K cal/ g mole) | $S^{\circ}$ 298 Cal/mole | Cp* Cal/g mole $^{\circ}K$ |
|---|---|---|---|---|
| Anthracene (s) | 30.87 | 68.30 | 49.58 | |
| Anthracene (g) | 55.17 | - | - | |
| Phenanthrene (s) | 27.76 | 64.87 | 50.63 | |
| Phenanthrene (g) | 49.46 | 73.21 (Est) | - | 46.4 |
| Naphthalene (g) | 36.08 | 53.44 | 80.22 | |
| Naphthalene (s) | 18.66 | 48.05 | 39.89 | |

The estimated standard Gibbs free energy of formation of phenanthrene gas was calcualated from the solid phase value using the solid phase heat capacity data (6) and other thermodymanic parameters. The ideal gas heat capacity of phenanthrene was estimated from using the group contribution method of Sounders.

The temperature dependence of heat capacity calculations are expressed in equation 1. (7).

$$Cp^* = -20.000 + (28.018 \times 10^{-2})\ T + (-21.062 \times 10^{-5})\ T^2 + (61.188 \times 10^{-9})\ T^3 \quad \text{---------}$$

Where Cp*, the ideal heat capacity, is expressed in cal/gmole $^{o}K$ and T, the temperature, in $^{o}K$. Similar thermodynamic data for cracked products such as benzene, toluene, etc. were obtained from standard handbooks.

Thermodynamic equilibria for the hydrogenation of a number of polycyclic aromatics including phenanthrene has been reported by Frye (8,9). This calculations of equilibrium data for phenanthrene hydrocracking reactions are summarized in figure 1. Some of the informative plots of equilibrium yields as a function of temperature and pressure are presented in Figures 2-4*. From Figure 2, it is apparent that from the thermodynamaic point of view, phenanthrene can be hydrocracked to form toluene in high yields at moderately severe temperatures (up to about 800$^{o}$F). At higher temperatures the equilibrium becomes increasingly less favorable, and other reactions such as the conversion of phenanthrene to benzene takes place as is evident from the equilibrium data plotted in Figure 3. This reaction os thermodynamically favourable at temperatures approaching 1400$^{o}$F and high conversions are feaaible at near atmospheric pressure in this temperature range.

Considering that the mechanism for the conversion reactions of condensed polyaromatics will undoubtedly involve hydrogenation steps, the hydrogenation reactions become very

important. The hydrogenation steps are highly temperature dependent with the result that the equilibrium concentration of hydrogenated products may be quite low at reaction conditions. Equilibrium calculation of some hydrogenation reactions are presented in Figure 4. Under non-equilibrium conditions, the extent of conversion is limited by reaction kinetics, as thermodynamic data does indicate the feasibility of the reaction, so that the final hydrogenation products depend upon the particular catalyst used (i.e. in this study sulfided Ni-W and sulfided Co-Mo catalysts).

*These calculations assume that the reaction mixture is an ideal gas.

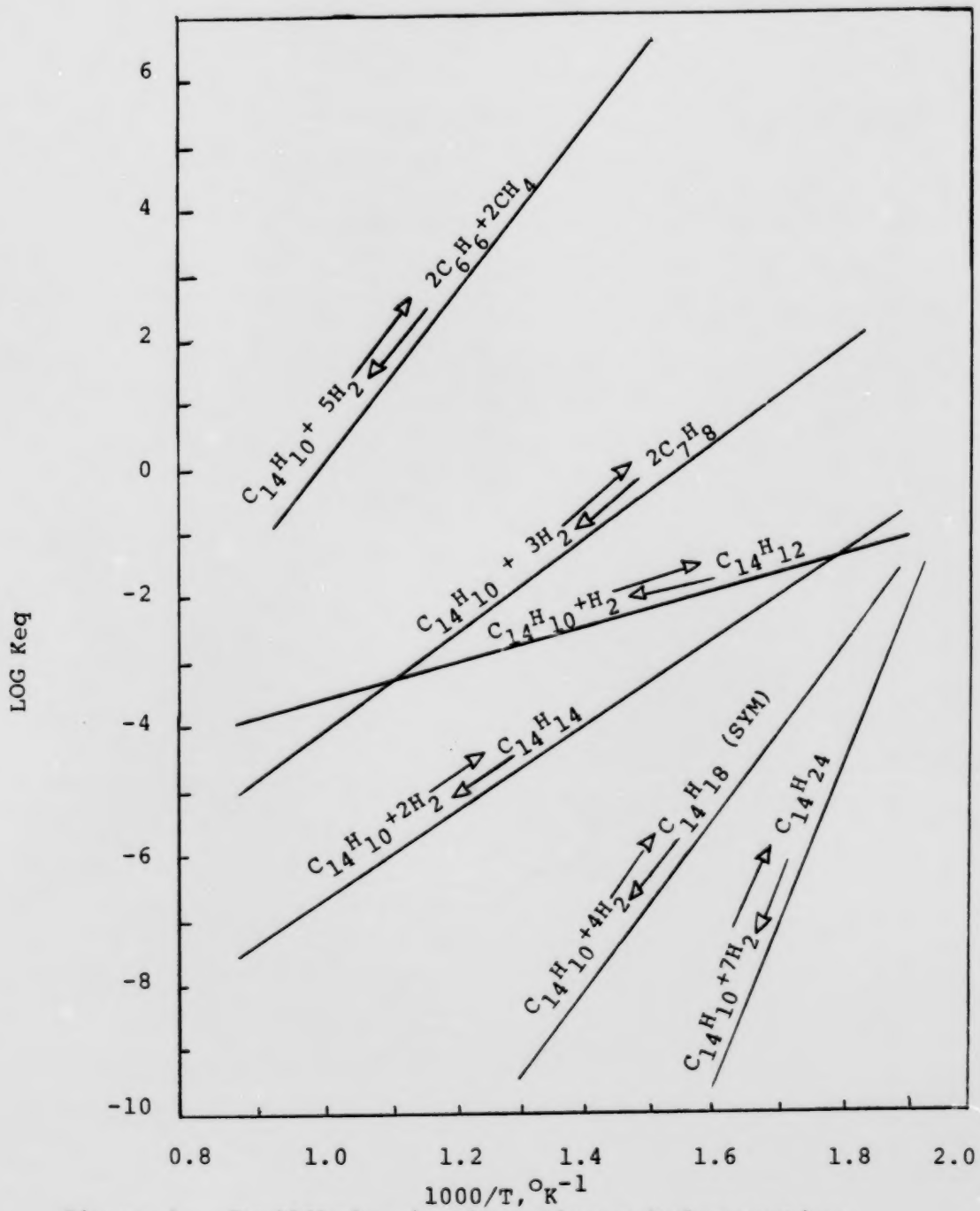



Figure 1. Equilibrium in phenanthrene hydrogenation reactions.

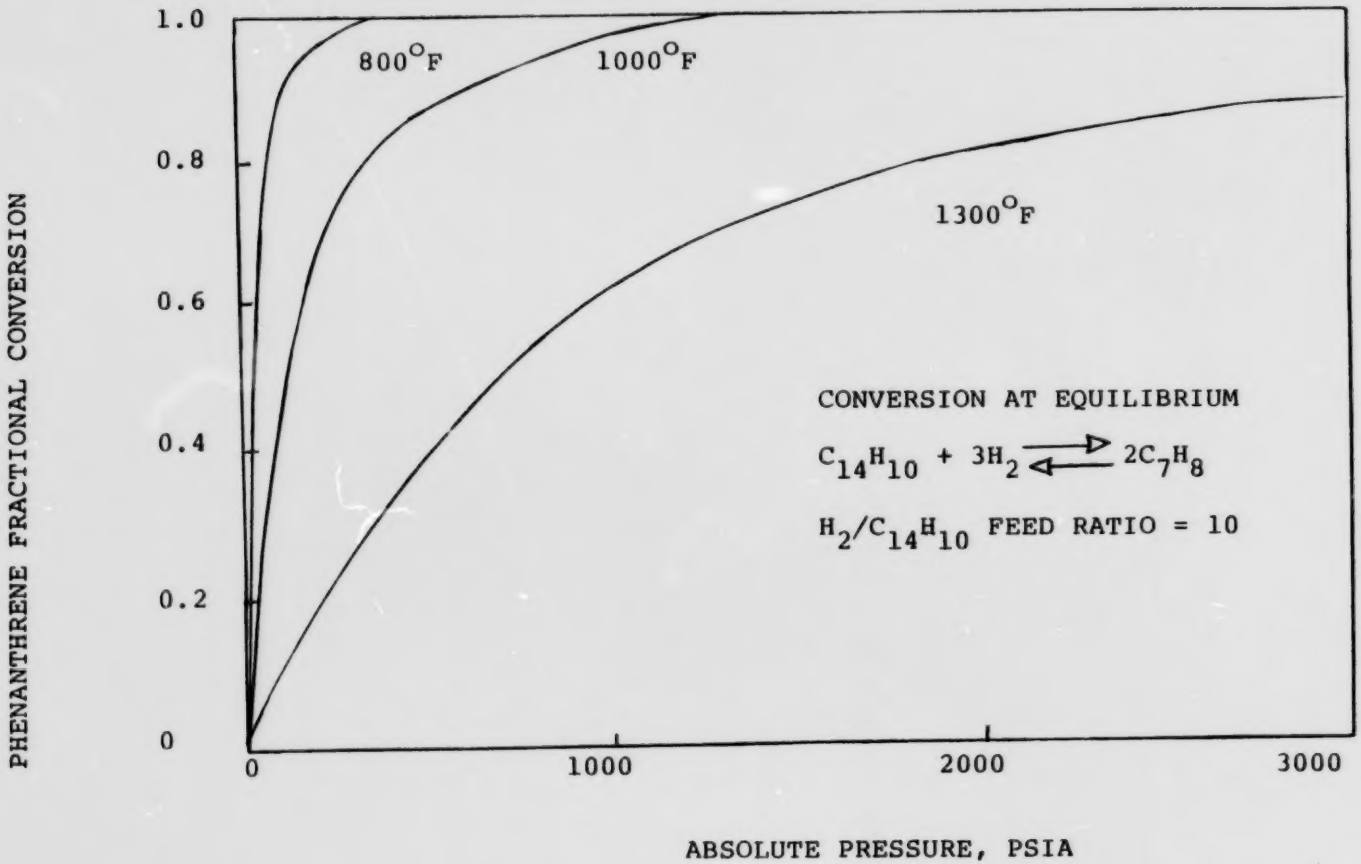



Figure 2. Equilibrium in the system $C_{14}H_{10}$, $C_7H_8$.

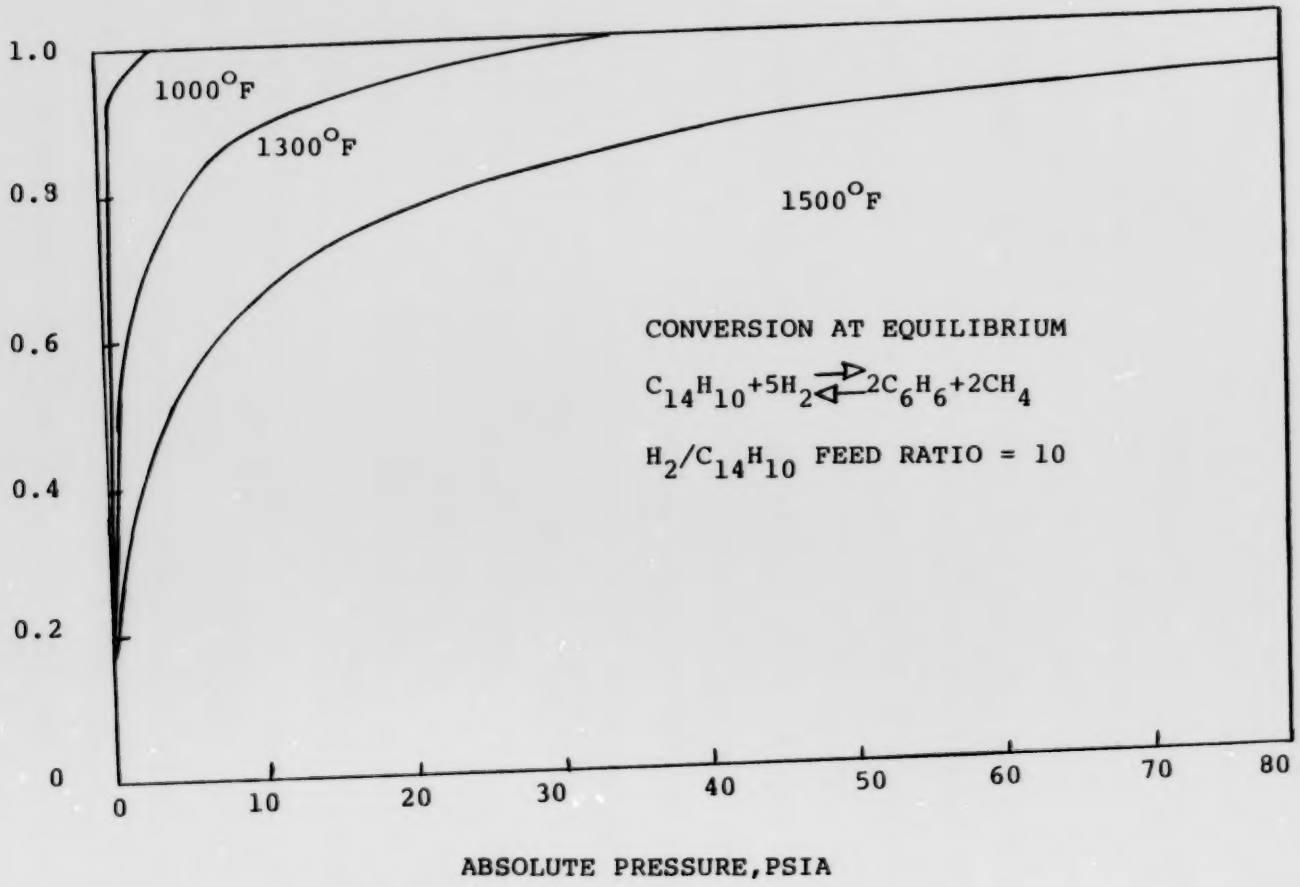



Figure 3. Equilibrium in the system $C_{14}H_{10}$, $H_2$, $C_6H_6$, $CH_4$.

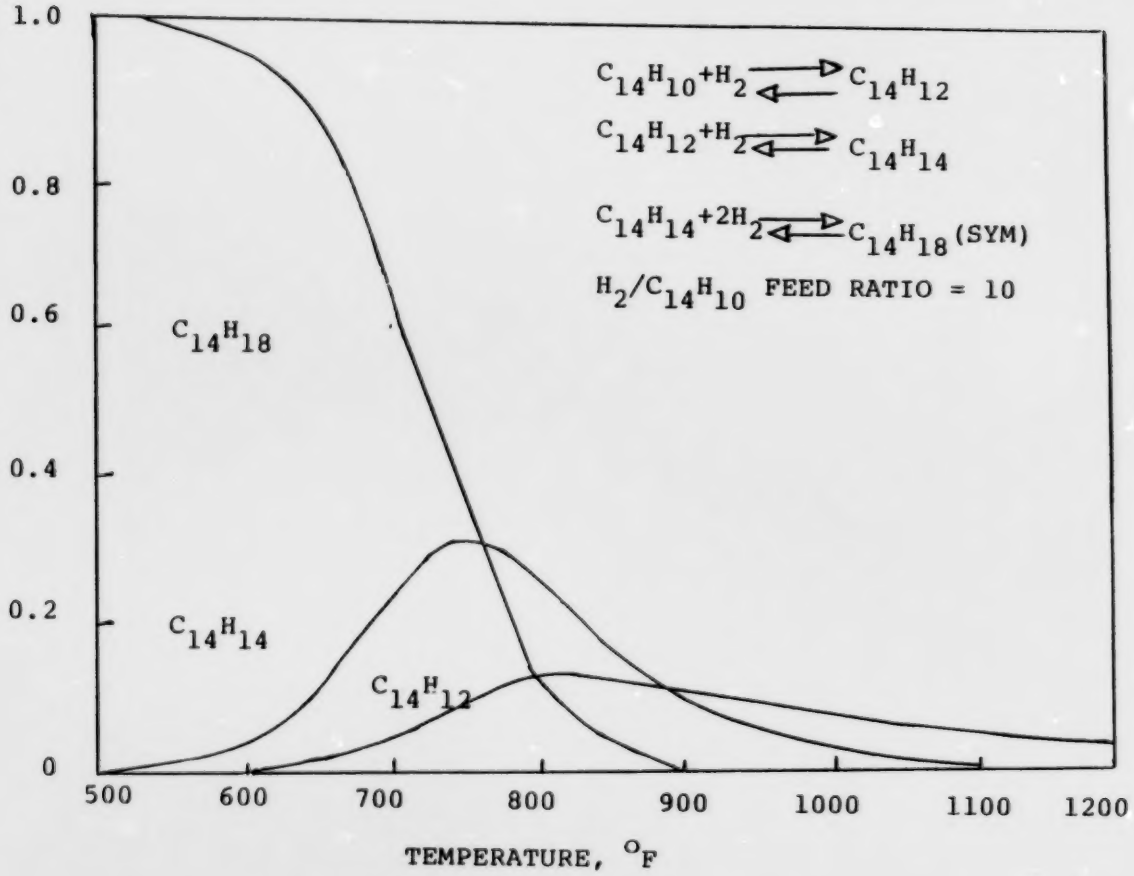
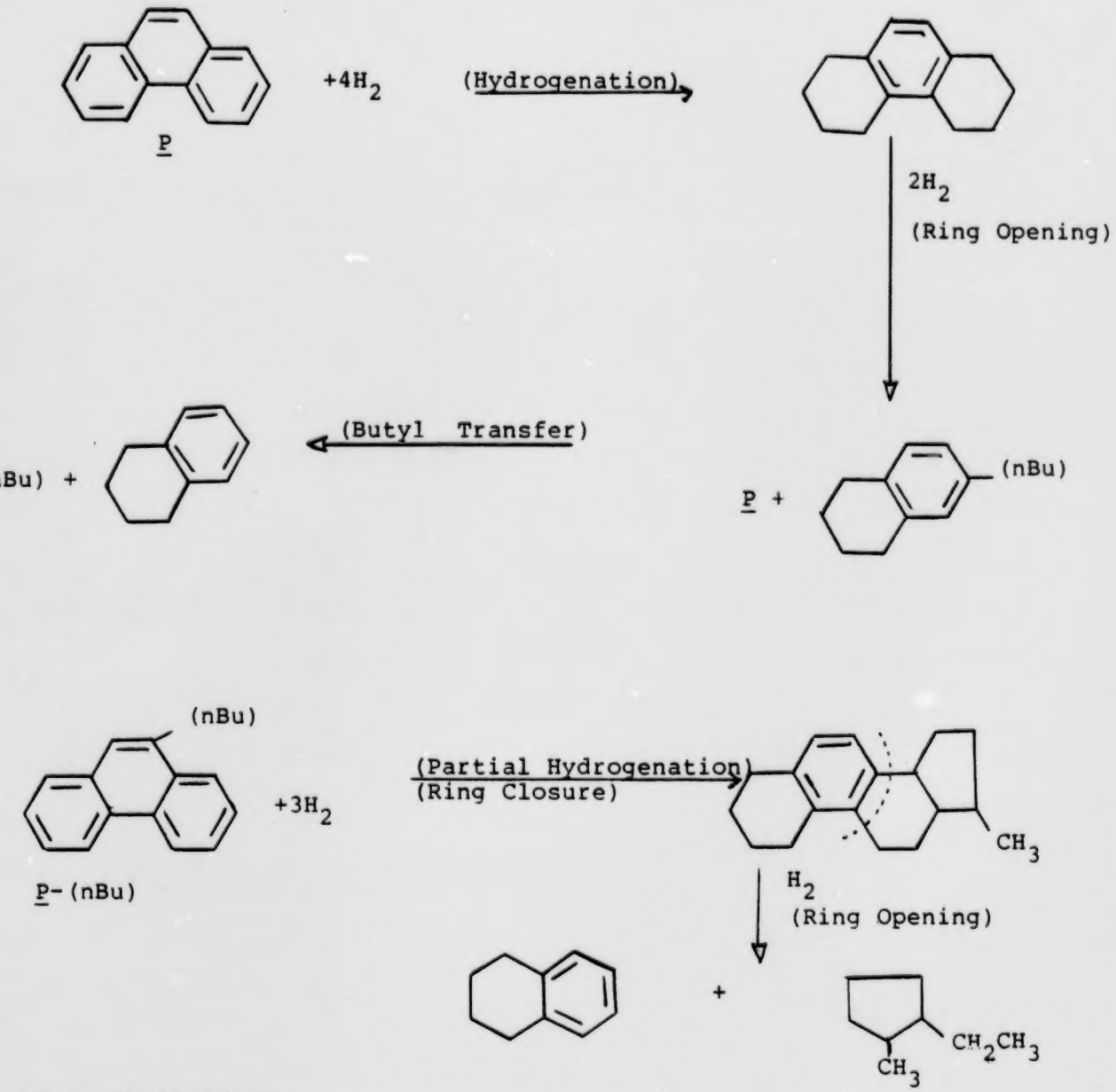



Figure 4. Equilibrium in the system $C_{14}H_{10}$, $H_2$, $C_{14}H_{12}$, $C_{14}H_{14}$, $C_{14}H_{18}$, P=1000 psig.

## III CATALYTIC HYDROGENATION, HYDROGENOLYSIS OF MODEL COMPOUNDS

Early work on the catalytic hydrogenation of polyaromatic compounds has been summarized by Smith (10). Active catalysts include the Group VIII transition metals in various reduced forms, oxides and sulfides of molybdenum and tugsten and copper in both the reduced form and as cupric acid oxide. Several observation deserve comment and are common to all the catalysts studied. First, the hydrogenation reactions generally take place in a stepwise fashion so as to maintain a maximum resonance in any intermediate product even if this involves a shift in unsaturation from one ring to another. Taking anthracene as an example, the first hydrogenation product is observed to be 9, 10 dihydroanthracene, with the tetrahydro, octahydro and perhydro derivatives produced upon further hydrogenation. Phenanthrene is hydrogenated in a similar fashion. A second observation is that the ease of hydrogenation tends to increase with increasing size of the molecule. For example the relative rates of hydrogenation of benzene, naphthalene and anthracene over sulfided tungsten catalyst were reported to be 100, 2300 and 6187 respectively. The hydrogenation of the final ring generally proceeds with some difficulty. Sullivan and coworkers hydrocracked phenanthrenes over nickel sulfided/silica-alumina catalysts in a fixed bed flow reactor (11, 12). Under conditions which gave low conversion, tetralin was the major product, but only traces of light alkanes were formed. A mechanism as depicted in Figure

5, involving partial hydrogenation, ring opening and transfer of a butyl group to another reactant molecule was postulated to explain the absence of large quantities of butanes in the products.



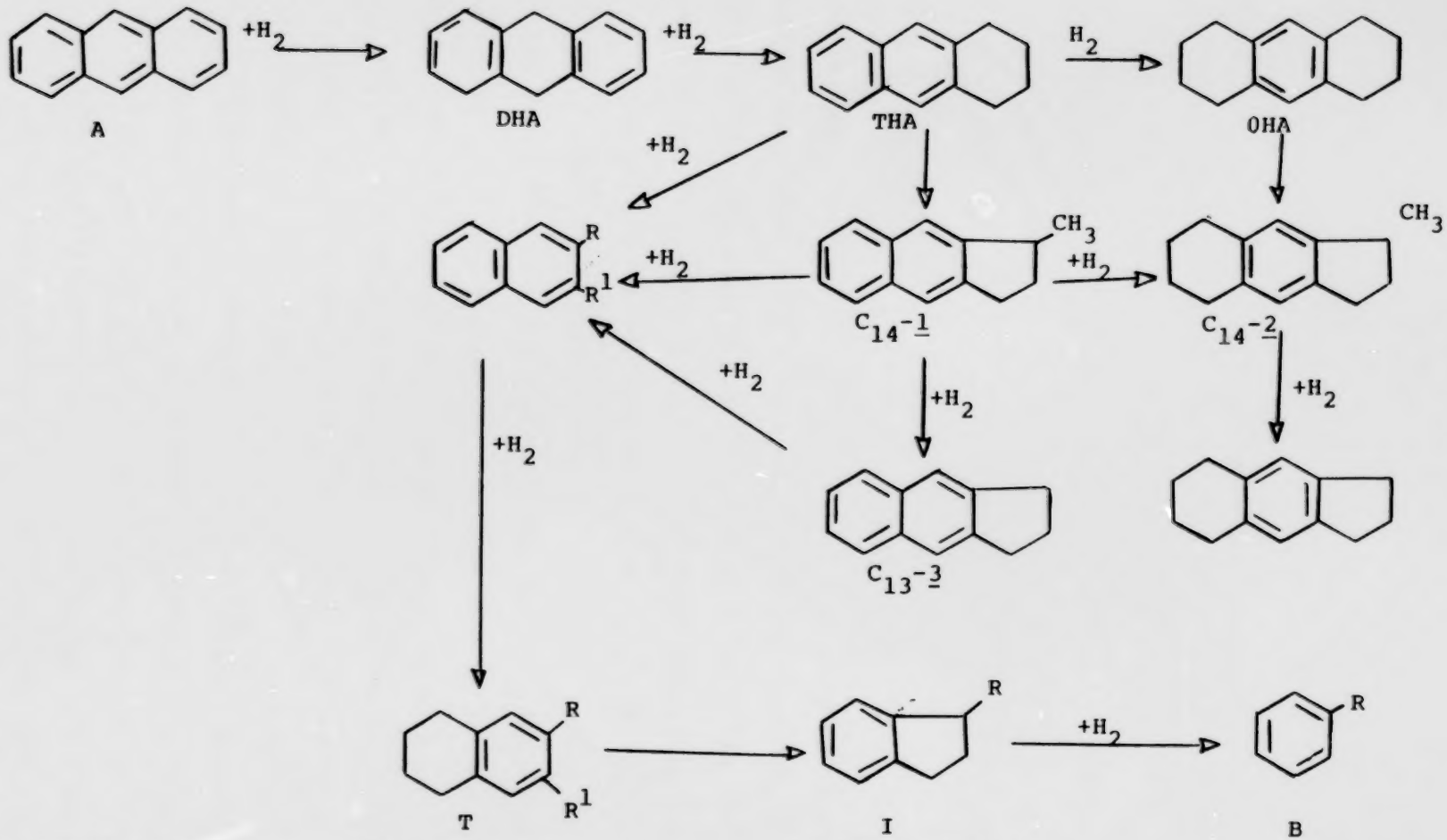

nBu= $CH_2CH_2CH_2CH_3$,

Figure 5- Butyl Transfer Mechanism of Sullivan (11)

Qader and coworkers hydrocracked naphthalene and anthracene over dual functional catalysts composed of the oxides of molybdenum, cobalt and nickel on silica-alumina (13, 14) with the main products observed being hydrogenated anthracene and naphthalene. The experiments were conducted in batch autoclaves. They later reported the hydrocracking of naphthalene, anthracene and pyrene over catalysts consisting of a physical mixture of a hydrogenation component (sulfides and oxides of Co, Mo, Ni and W) and a silica-alumina catalyst (15, 16). Anthracene was hydrogenated and cracked to naphthalene derivatives which were subsequently cracked to benzenes. Similarly, pyrene was hydrocracked by a path which involved the formation of phenanthrene, which was in turn hydrocracked to naphthalene and ultimately to benzene.

The cracking reactions were accompanied by considerable isomerizations of saturated six member rings to methyl substituted five member rings. Such isomerizations are commonly observed in the presence of acidic catalysts, the mechanism for the hydrocracking of anthracene is explained in Figure 6.

Von Rumohrs and Koelling studied the hydrogenolysis of anthracene and phenanthrene over supported nickel catalysts in a flow reactor at atmospheric pressure (17). A mechanism invlolving saturation and cracking of adjacent rings was postulated to explain the scarcity of benzene in the products.




A= Anthracene
$C_{14}$-1, $C_{14}$-2 = DHA= Dihydro $C_{14}$- Isomers
T= Tetralins
I= Indanes

THA= Tetrahydro
$C_{13}$-3, $C_{13}$-4 = OHA= Octahydro $C_{13}$- Ismoers
B= Benzenes
R= $R^1$= Methyl groups

Figure 6- Mechanism for Hydrocraking of Anthracene, Qader (16)

Strong Lewis catalysts such as zinc chloride and aluminum bromide are active for the conversion of coal, and coal extract when used in large amounts, e.g. a one-to-one catalyst-to-reactant weight ratio (18,19). One interesting feature of the zinc chloride hydrocracking of polynuclear hydrocarbons is the high selectivity to products boiling in the gasoline range (18). Pyrene was hydrocracked to give high yields of naphtha range products.

As should be apparent from the discussion above, most studies on the hydrocracking of polyaromatics have utilized catalysts which include an acidic component, and consequently the cracking mechanism has generally been one involving carbonium ion intermediates. One would expect a substantially different product distribution from cracking by a path which involved free radicals. Carbonium ion and free radical mechanisms have been compared in early reviews (20,21).

Some insight into the types of products that might be obtained via a free radical hydrogenolysis of polynuclear aromatic compounds can be found in the study of Penninger and Slotboom who investigated the high pressure thermal hydrogenolysis of phenanthrene and anthracene (22). They found that both tricyclics are cracked mainly by stepwise hydrogenation of outer rings, ring opening and side chain cracking. Cracking within the side chain was extensive in contrast to the dealkylation of side chains normally observed over acidic catalysts. The path involving intermediate 1

dominates the reaction sequence since no 1 -subsituted napthalenes were detected, as depicted in Figure 7. In addition to terminal ring cleavage, they observed substantial quantities of ethylbiphenyl, biphenyl, and diphenylethane in their cracked products suggesting cracking at the central rings according to the scheme of Figure 8. The path involving the ethylbiphenyl radical is preferred. In a recent report Showronski and Recht (23) hydrocracked phenanthrene in the presence of a 50/50 mixture of $MOH/M_2CO_3$(M=Li, Na,K) in a batch autoclave at 475$^{o}$C and 3000 psi. A large ratio (6/1) of catalyst to phenanthrene was employed and reaction times were varied up to one hour. While considerable hydrogenation and ring opening reactions were observed, the conversion to cracked product was low. The product distribution was similar to the thermal data of Penninger and Slotboom (22) as depicted in Figure 8. The cracked products were mostly alkynaphthalenes Substantial amounts of 2- ethylbiphenyl and smaller quantities of diphenylethane were also present.

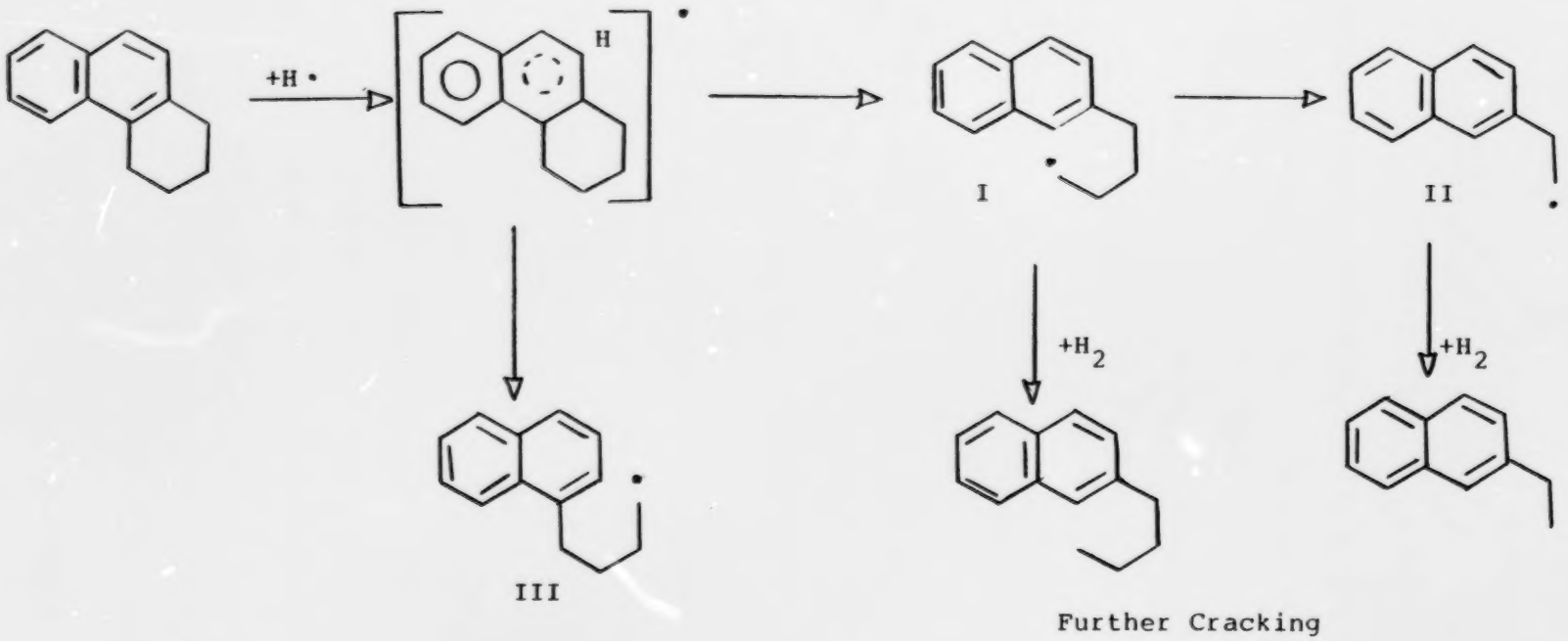



Figure 7- Thermal Hydrogenolosis of Tetrahydro Phenanthrene., Penninger and Slotboom (22)

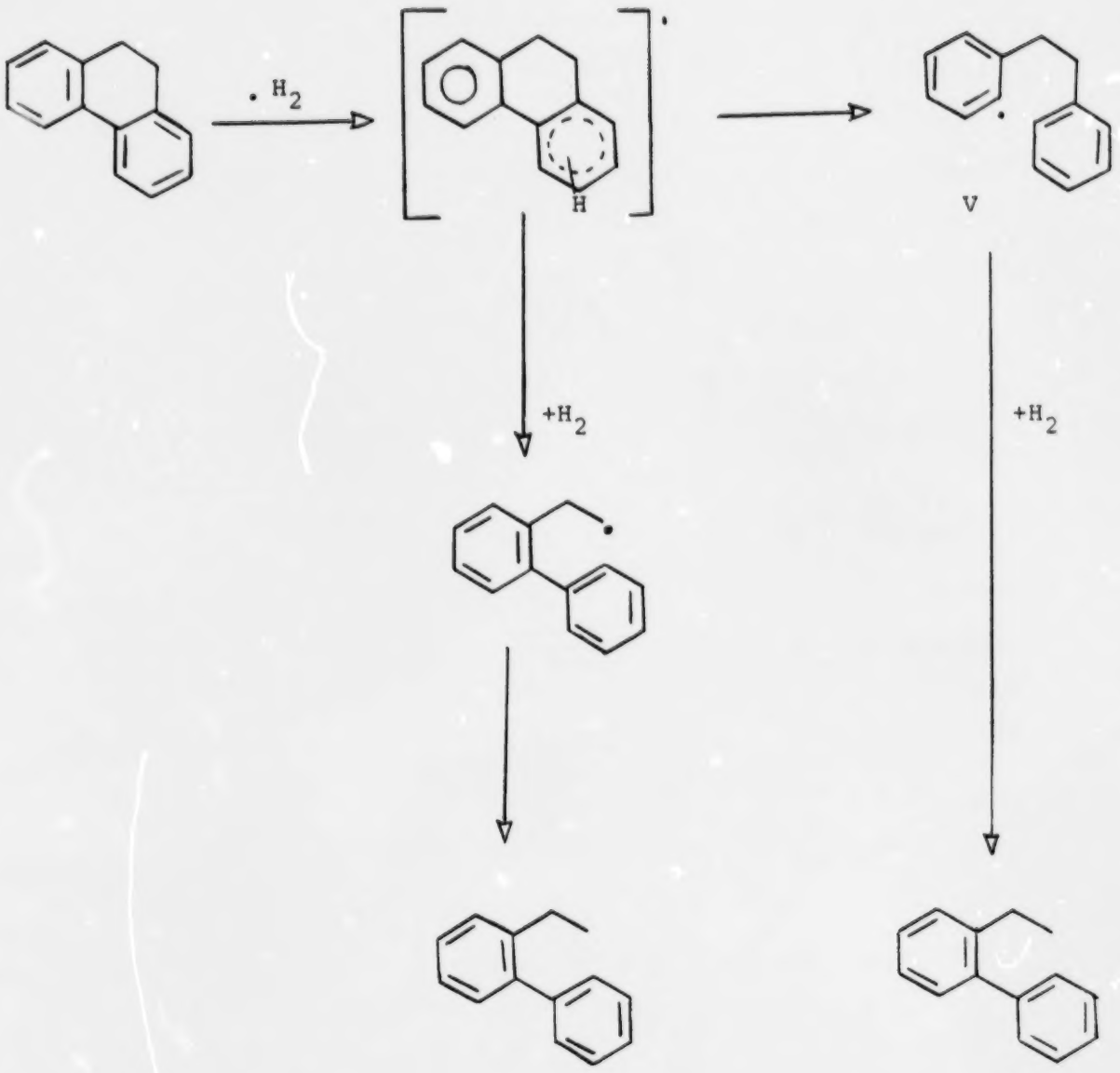



Figure 8: Thermal Hydrogenolysis of Dihydrophenanthrene, Penninger and Slotboom (22)

# IV EXPERIMENTAL

## Flash Hydro Pyrolysis Apparatus

The assembly of the pressurized reactor and associated components depicted schematically in figure 9 was designed and assembled for this project. It was considered a major accomplishment in view of considerable research and time expended and cost incurred in the engineering aspect. Various designs and approaches had to be discarded for the flash heating system and control. Because of the long delivery delays for specialized components from the U.S. and because of mail strike in Canada some of our significant efforts were hampered at every step and the control circuits had to be re-designed to utilize the readily available items.

The FHP reactor consists of a 0.25" diameter x 15" long 304 stainless steel tube with a wall thickness of 0.035". Swagelok fittings are attached at each end and a type K thermocouple spot welded 6" from one end.

It is held in place by clamps, one of which, at the right, is also an electrical connection for the heating power supply. The left end of the reactor tube is held loosely to allow for expansion when it is heated. A removable electrical connection E completes the circuit for the resistance heating of the tube and is generally placed at a position such that the thermocouple is midway between it and the other fixed electrical connection.

The tube is heated rapidly by passing a large current through it and the temperature monitored by means of a digital thermometer linearized for use with a type K thermocouple. The heating current is controlled by the switching control unit which consists of a series of solenoids actuated by timers T1 and T2 in the central control unit. A manual switch in the main heating control circuit can be used to disconnect the main power in the event that the solenoids in the main heating power supply circuit become welded and the reaction tube overheats.

The main heating which heats the tube rapidly is controlled by timer T1 in the central unit and the secondary heating which uses a lower voltage power supply to maintain the temperature for an extended period if necessary (2 to 10 sec) is controlled by timer T2. The timers control unit to allow a large current from a bank of heavy duty batteries to pass through the reactor tube. The battery voltage for the secondary heating power supply is switch selectable at 2 to 12 volts while the main heating power supply voltage is changed by repositioning the positive battery terminal clamps.

Typical Experimental Run.

During an experimental run, the cleaned and dried reactor tube and trap are first connected to the flow control system and the clamps and electrical connections attached. An approximately 10 mg sample is weighed accurately in a

boat and mixed with a roughly equal amount of catalyst. Additional catalyst is tamped down on top of the catalyst sample mixture and the boat weighed again. Approximately 50 to 80 mg of catalyst is used.

The sample boat is inserted into the reactor tube at the thermocouple position by disconnecting the S tube at swagelok fitting SF1, inserting the boat with forceps and pushing it through the tube to the thermocouple position with a stainless steel rod. The fitting SF1 is then re-connected and the system pressurized to 75 psig with nitrogen. The system is flushed with nitrogen for about 5 Minutes and tested for leaks, pressurized with hydrogen at 1000 psig, checked for leaks again and the swagelok fittings tightened if necessary.

The hydrogen flow rate is adjusted to the desired value using metering value MV5. The coiled trap is inserted into a dryice/acetone dewar and a plexiglas shield put in place in front of the entire pressurized system. After about 5 minutes of flushing with hydrogen to displace the nitrogen, the heating system is actuated and the maximum temperature is noted.

The hydrogen cylinder metering valve MV1 is then closed and the pressure allowed to drop. The plexiglas shield is removed and metering valves MV2 and MV5 are closed when the flow rate has dropped to zero. The system is

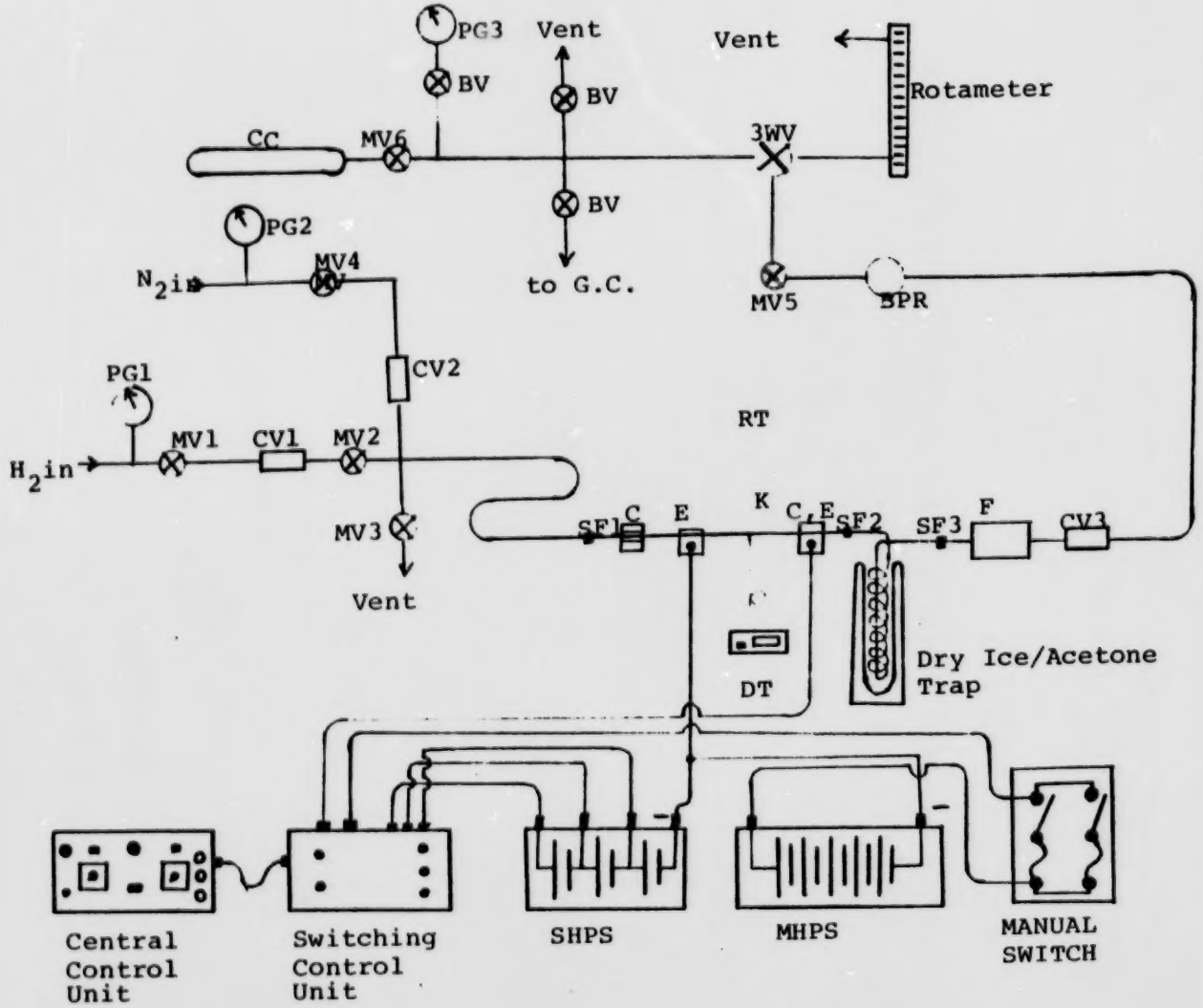
then slowly pressurized to 75 psig with nitrogen, MV5 is opened slightly and the hydrogen flushed out for 5 minutes. The nitrogen cylinder metering valve MV4 is closed, the flow rate allowed to drop to zero then MV5 is closed. The reactor tube and trap are then dismantled and removed.

The sample boat is pushed out of the reactor tube and discarded. The reactor tube and trap are them rinsed several times with carbon disulfide. The $CS_2$ volume is made up to 10 ml in a volumetric flask and 3 µl samples of this solution injected into the gas chromatograph for analysis. The reactor tube and trap are rinsed thoroughly with hexane and acetone and dried by passing air through with a water aspirator.

## Notations for Figure 9

| | |
|---|---|
| PG. | Pressure Gauge |
| MV. | Metering Valve |
| CV. | Check Valve |
| SF. | Swagelok Fitting |
| F | Filter |
| BPR | Back Pressure Regulator |
| 3WV | 3-way valve |
| BV | Ball Valve |
| CC | Collection Cylinder |
| RT. | Reaction Tube |
| C | Clamp |
| E | Electrical Connection |
| K | Type K Thermocouple |
| DT. | Digital Thermometer |
| T | Timer |
| SHPS | Secondary Heating Power Supply |
| MHPS | Main Heating Power Supply |

Flow Diagram of F H P Apparatus



Safety Features

- The entire system has been pressure tested.
- The heating control is custom designed. The system employs a solid state timing modules and electro-mechanical sequenced switches.
- All circuitary is solid state and sealed against open spark hazards
- The reactor, collection system and valves facing the operator has been mounted on a 4 x 5½ foot board. Through flexa frame foot plates the system can be enclosed in a thick transparent plexiglass with access holes to the valves for their manipulations.

Sulfiding of the Catalysts

Three batches each of the cobalt molybdate catalyst and of the nickel tungsten catalyst were sulfided. The oxide forms of the catalysts obtained from Harshaw Chemicals Co., Ohio were ground with mortar and pestle and packed into a 15 inch long and ¼ inch OD stainless steel reaction tube plugged at each end with glass wool. The tube was heated to 400°C for various times while passing a stream of 10% $H_2S$ in $H_2$ through the tube.

Briefly the following procedure for sulfiding the catalysts was used: The tube filled with catalyst was inserted into the flow control system with sewage lock fittings and nitrogen passes through at room temperature and 80 psig. After the system was tested for leaks, the $N_2$ was turned off

at the cylinder and 10% $H_2S$ passed through room temperature at 75 psig. The tube was then rapidly heated (in 5 Minutes) to 400°C and left at 400°C for the indicated reaction time. The heat was then turned off and the tube cooled to room temperature before switching the flow back to $N_2$. After a further 15 minutes of flushing with $N_2$ the gas was removed from the flow system. The sulfided catalyst was then removed from the tube and stored in glass stoppered vials. The catalysts were analyzed for sulfur content and are reported in Table 2.

TABLE 2

Sulfur Content in the Sulfided Catalyst

| Catalyst Cat. No | Stated Composition | Reaction Time (Min) | $H_2S$ Flow Rate (ml/min) | %S Found |
|---|---|---|---|---|
| (1) CO MO-0402 +1/8 | 3% CoO, 12% Mo $O_3$ | 5 | 100 | 2.94 |
| | on $Al_2O_3$ | 30 | 100 | 3.52 |
| | | 180 | 150 | 8.07* |
| (ii) Ni-430 1E 1/12 | 6% NiO | 2 | 250 | 4.83 |
| | 19% $WO_3$ | 30 | 250 | 7.19 |
| | on $Al_2O_3$ | 180 | 250 | 10.42** |

* Theoritical Max = 9.30%S
** Theoritical Max =10.46%S

Method for Sulfur Analysis in Sulfided Catalysts

One gram of AR anhydrons $Na_2 CO_3$ was placed in iron crucible and 0.4 - 0.5 gram of catalyst was accurately weighed into it. About 5-6 gram of sodium perioxide was added and mixed well with glass rod. The covered crucible was heated to 600°C in the muffle furnace for about 15 minutes. The frunace was allowed to cool to room temperature and the contents extracted with distilled water in a covered 600 ml beaker. The crucible contents were completely removed and the solution diluted to 300 ml of conc HCL added with stirring. The solution was filtered through whatman #40 filter paper and washed 10 times with 15 ml portion of hot 1% $Na_2CO_3$ solution.

Concentrated HCL was added to the combined filterate and washings in a 1 litre beaker until acid to methyl red and 2 ml added in excess. The solution was diluted to 600 ml heated to boiling and stirred vigorously as 5 ml of hot 10% $BaCl_2$ solution was added dropwise from a burette. The solution was kept hot but not boiling for 1 hour in a covered beaker and filtered through whatman #40 filter paper. The filterate was tested with $BaCl_2$to determine if further precipitations could occur. The ppt was washed free of chloride ions until 5 ml of filterate gave negative test with silver nitrate solution. The precipitate was dried and ignited with gradual heating with a previously ignited and weighed crucible. The %S was calculated.

Future Sulfiding of Catalysts

Thus for both the catalysts it was considered that the sulfiding reaction will be complete at 250 ml/min for a reaction time 180 minutes. In all experiments a minumum of 180 minute reaction time was allowed at a flow rate of 250 ml/minute.

## APPARATUS OPERATIONAL DIFFICULTIES

Numerous problems were encountered in the inial phases of this investigation and as a consequence the results obtained are quite limited.

(a) Reactor Heating Tests

In initial tests at high current several reactor tubes melted down. It was found that solenoid contacts welded in a closed position, after the timer had turned off. However, pushing the main DC power switch which deactivates the mainpower solenoid when it becomes apparent that the reactor is overheating, prevented this problem. To prevent the sticking of solenoid under high current the heavior duty relays with silver plated contacts were used in future. Later the circuit was amended to automatically disconnect the main power in the event the solenoids in the main heating power supply became welded and reaction tube started overheating. A precautionary manual switch was also installed.

(b) Corrosion Problem

It was found that the sulfiding gas (10% $H_2S$ -90% $H_2$) was extremely corrosive to some part of the apparatus, Hydrogen sulfide in the presence of moisture is known to corrode type 304 stainless steel. Numerous leaks were encountered in pressure gauge valves and fittings not made of 316 stainless steel (which is resistant to $H_2S$ in the presence of moisture). O-ring failures with the metering valve occured on several occasions resulting in a sudden and rapid depressurization of the system, and making it necessary to terminate the run and begin again with fresh catalyst.

At later stages the needle valve of the flowmeter had to be disassembled and replaced.

Despite the numerous problems encountered during the course of this investigation a total of thirty runs were completed on phenanthrene and ten each of anthracene and naphthalene. Unfortuantely much of the time was spent on the analytical procedure after the apparatus difficulties were sloved.

Materials

Phenanthrene (98% purity, melting point 99-101$^{o}$C according to the supplier) was purchased from Aldrich Chemical Company. An elemental analysis by Guelph Chemical Laboratories indicated that the sample contained 94.16% carbon, 5.56% Hydrogen, 0.18% nitrogen and 0.44% Sulphur.

Anthracene and Naphthalene were obtained from Aldrich Chemical Company and purified by crystalization. An elemental analysis was done at Guelph Chemical Laboratories. For anthracene carbon was found 94.64%, hydrogen 6.32% and nitrogen 0.00%. For Naphthalene C= 93.64%, H= 6.32% and N= 0.00%. These results indicated that anthracene and napthalene were in high purity.

High purity hydrogen (99.995%). Hydrogen- hydrogen sulphide mixture (10% $H_2S$ in $H_2$) were obtained from Matheson in 3,500 psig cylinders. Both catalysts, the CO-MO and Ni-W were sulfided by the procedure given above.

Analytical Procedure

Carbon disulfide was used as a solvent to dissolve the products trapped in the cooling coil. The trap was washed

several times and made-up to 10 ml. The products were analyzed on a Hewlett Packard Gas Chromatograph, Model 5831, a dual column gas chromatograph possessing a linear temperature programming capabality with a flame ionization detector, using nitrogen a carrier gas. The operating conditions are presented in Table 3.

TABLE 3

Conditions for Gas Chromatographic Analysis

| | | |
|---|---|---|
| Column: | 6 ft. x ¼" Stainless Steel packed with 5% SE-30 on 60/80 mesh chromosorb P, AW | |
| Carrier Gas | : | Nitrogen |
| Flow Rate | : | 30 ml/min |
| Detector Temperature | : | 275°C |
| Injector Temperature | : | 275°C |
| Oven Temperature | : | 180°C |
| Sample Size | : | 3 ul |

Prior to undertaking the quantitative analysis of the products it was necessary to check the linearity of the detector and the percent recovery of the products. The linearity of the detector was checked by injecting solutions of sample in carbon disulfide at different concentrations and plotting the observed area vs the sample concentrations in ppm.

The recovery studies was accomplished using pure compound and subjecting it to similar experimental conditions described

above but without catalyst.

During the initial recovery it was found that only 5-25% of the phenanthrene was recovered; this was due to its condensation on the line between the heating tube and the cooling coil, even though the line was heated. It was then decided to place the dry ice trap immediately after the reaction tube, and extract both the reaction tube and the trap with carbon disulfide. The recovery studies then showed more than 95% values as shown in the result section.

## V RESULTS

The hydrogenation of phenanthrene over sulfided Ni-W catalyst and sulfided Co-M0 catalyst are presented in tables 4 to 10. The results of hydrogenation of anthracene and naphtahalene are given in tables 11, 12, 13 and 14 respectively. The majority of experiments have been limited to conditions emphasizing a pressure of 1000 psi, a reaction temperature of about 500°C, an average hydrogen flow rate of 1.18 ml/sec and residence time of 1 and 2 seconds.

The products that we have been able to quantify is the the phenanthrene (P ), and dihydro phenanthrene (D H P) using external standards. These compounds were obtained from Aldrich Chemical Company. Other standards were not readily available from suppliers. Between the peaks of P and D H P, there are two other products that have been identified as Tetrahydro phenanthrene (T H P) and Octahydro phenanthrene (O H P). Several chromatograms of condensible products at dry ice bath are given in figures 10 to 18.

A standard sample is also included for comparison. As mentioned earlier only dihydrophenanthrene standard was available. The tetrahydro and octahydro phenanthrene peaks inially assigned were later confirmed by gas chromatograph-mass spectrometric analysis.

TABLE 4

Hydrogenation of Phenanthrene over Sulfided Ni-W/Catalyst.

| Run No. | Initial Conc. of Phenanthrene(in moles) | Catalyst/P Ratio(wt/wt) | Reaction Temp. (°C) | $PH_2$ (psi) | Reaction Products (% Moles) P | DHP | Reaction Products THP | OHP | Conversion % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0752 | 3.73 | 580 | 1000 | 67.6 | 0.15 | - | - | 32.4 ? |
| 2 | 0.0478 | 5.82 | 567 | 1000 | 17.8 | 6.40 | 1.07 | 1.0 | 82.2 |
| 3 | 0.0637 | 5.84 | 490 | 1000 | 24.4 | 0.74 | 2.5 | 1.0 | 75.6 |
| 4 | 0.0521 | 6.70 | 490 | 1000 | 2.1 | 0.04 | - | - | 97.9 |
| 5 | 0.0644 | 5.67 | 501 | 1000 | 8.3 | 2.97 | 2.41 | 1.0 | 91.7 |
| 6 | 0.0588 | 7.50 | 494 | 1000 | 7.3 | 3.46 | 2.67 | 1.1 | 92.7 |
| 7 | 0.0554 | 7.59 | 501 | 1000 | 11.4 | 3.90 | 3.19 | 1.0 | 88.6 |
| 8 | 0.0604 | 6.59 | 464 | 1000 | 13.4 | 3.93 | 2.30 | 1.0 | 86.6 |
| 9 | 0.0561 | 6.78 | 448 | 1000 | 6.6 | 5.51 | 4.25 | 1.0 | 93.4 |
| 10 | 0.0549 | 8.44 | 516 | 1000 | 6.1 | 2.65 | 1.92 | 1.0 | 93.9 |

*P=Phenanthrene, DHP=Dihydro pehanthrene, THP=Tetrahydro phenanthrene
OHP=Octahydro phenanthrene.

TABLE 5

Hydrogenation of Phenanthrene over Sulfided Co-Mo/Catalyst

| Run No. | Initial Conc. of Phenanthrene (m.moles) | Catalyst/P Ratio(wt/wt) | Reaction Temp. (°C) | $PH_2$ (psi) | Reaction Products (Moles %) P | DHP | THP | OHP | Reaction Yield % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0577 | 6.07 | 587 | 1000 | 10.4 | 0.15 | 3.5 | 2.0 | 89.6 |
| 2 | 0.0501 | 7.37 | 521 | 1000 | 19.6 | 5.24 | - | - | 80.4 |
| 3 | 0.0672 | 5.19 | 504 | 1000 | 22.0 | 0.82 | 2.5 | 1.5 | 78.0 |
| 4 | 0.0689 | 4.92 | 490 | 1000 | 24.4 | 0.74 | 1.09 | 0.80 | 75.6 |
| 5 | 0.0561 | 6.00 | 432 | 1000 | 15.5 | 2.88 | 1.55 | 1.09 | 84.5 |
| 6 | 0.0652 | 6.67 | 503 | 1000 | 22.6 | 6.45 | 8.21 | 3.37 | 77.4 |
| 7 | 0.0594 | 6.36 | 515 | 1000 | 24.5 | 6.57 | 5.11 | 2.02 | 75.5 |
| 8 | 0.0667 | 6.38 | 501 | 1000 | 12.9 | 5.14 | 4.68 | 1.57 | 87.1 |
| 9 | 0.0525 | 7.75 | 525 | 1000 | 12.1 | 7.37 | 5.41 | 6.50 | 87.9 |
| 10 | 0.0713 | 5.47 | 507 | 1000 | 9.8 | 2.85 | 2.39 | 1.00 | 90.2 |

*P=Phenanthrene, DHP=Dihydro phenanthrene, THP=Tetrahydro phenanthrene
OHP=Octahydro phenanthrene

TABLE 6

Hydrogenation of Phenanthrene without Catalyst

| Expt. No. | Residence Time (sec.) | Initial Conc. of Phenanthrene (m.moles) | Reaction Temp. (°C) | $pH_2$ (psi) | Reaction Products* | | | | Recovery of Phenanthrene % |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | P | DHP | THP | OHP | |
| 1 | 1 | 0.0615 | 694 | 1000 | 0.0638 | - | - | - | 103.7 |
| 2 | 1 | 0.0702 | 742 | 1000 | 0.0641 | - | - | - | 91.3 |
| 3 | 2 | 0.0521 | 631 | 1000 | 0.055 | - | - | - | 105.56 |

P = Phenanthrene, DHP = Dihydro phenanthrene,

THP = Tetrahydro phenanthrene, OHP = Octahydro phenanthrene.

TABLE 7

Hydrogenation of Phenanthrene over sulfided Ni-W Catalyst# (Repeated runs)

| Expt. No. | Residence Time (sec.) | Phenanthrene (m.moles) | Catalyst/P Ratio (wt/wt) | Reaction Temp ($^{o}$C) | $pH_2$ psi | Reaction Products*(%) | | | | Reaction yield(%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | P | DHP | THP | OHP | |
| 1 | 1 | 0.0609 | 7.05 | 512 | 1000 | 32.7 | 2.48 | 1.80 | - | 67.3 |
| 2 | 2 | 0.0515 | 8.48 | 479 | 1000 | 12.2 | 0.50 | 0.94 | - | 87.8 |

P = Phenanthrene, DHP = Dihydro phenanthrene,

THP = Tetrahydro phenanthrene, OHP = Octahydro phenanthrene.

# Freshly prepared catalyst.

TABLE 8

Hydrogenation of Phenanthrene over sulfided Ni-W Catalyst#

| Expt. No. | Residence Time (sec.) | Phenanthrene (m.moles) | Catalyst/P Ratio (wt/wt) | Reaction Temp. ($^{o}$C) | $pH_2$ psi | Reaction Products*(%) | | | | Reaction Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | P | DHP | THP | OHP | |
| 1 | 1 | 0.0638 | 7.14 | 702 | 1000 | 27.1 | 0.6 | - | - | 72.9 |
| 2 | 1 | 0.0521 | 7.84 | 680 | 1000 | 21.3 | 0.3 | - | - | 78.7 |
| 3 | 2 | 0.0593 | 7.45 | 647 | 1000 | 23.6 | 3.9 | 1.1 | - | 76.4 |
| 4 | 2 | 0.0543 | 7.95 | 640 | 1000 | 27.2 | 2.6 | 0.8 | - | 72.8 |

P = Phenanthrene, DHP = Dihydro phenanthrene,

THP = Tetrahydro phenanthrene, OHP = Octahydro phenanthrene

# New batch of catalyst.

TABLE 9

Hydrogenation of Phenanthrene over sulfided Co-Mo Catalyst#

| Expt. No. | Residence Time (sec.) | Phenanthrene (m.moles) | Catalyst/P Ratio (wt/wt) | Reaction Temp. ($^{o}C$) | $pH_2$ psi | Reaction Products(%) | | | | Reaction Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | P | DHP | THP | OHP | |
| 1 | 2 | 0.0449 | 11.37 | 598 | 1000 | 23.1 | 2.26 | 0.75 | - | 76.9 |
| 2 | 2 | 0.0603 | 7.47 | 621 | 1000 | 38.2 | 1.84 | 0.67 | 0.52 | 61.8 |

P = Phenanthrene, DHP = Dihydro phenanthrene,

THP = Tetrahydro phenanthrene, OHP = Octahydro phenanthrene.

# Old batch of Catalyst.

TABLE 10

Hydrogenation of Phenanthrene (Confirmation Runs)

over-sulfided Ni-W1 Catalyst.

| Expt. No. | Residence Time (Sec) | Phenanthrene ( in mmoles) | Catalyst/P ratio (wt/wt) | Reaction Temp. $^{o}C$ | $PH_2$ (psi) | % Unreacted Phenanthrene | % Total Reaction Yield |
|---|---|---|---|---|---|---|---|
| CR3 | 1 | 0.0435 | 11.17 | 460 | 1000 | 23.1 | 76.9 |
| CR4 | 1 | 0.0538 | 8.52 | 452 | 1000 | 23.1 | 76.9 |
| CR5 | 1 | 0.0571 | 7.25 | 489 | 1000 | 22.3 | 77.7 |

TABLE 11

Hydrogenation of Anthracene over Sulfided Ni-W/Catalyst

| Expt. No. | Residence Time(Sec) | Anthracene (m moles) | Catalyst/A ratio (wt/wt) | Reaction Temp. $^{o}C$ | $PH_2$ (psi) | % Unreacted Anthracene | % Total Reaction Yield |
|---|---|---|---|---|---|---|---|
| A1 | 1 | 0.0514 | No catalyst | 438* | 1000 | 93.7 | - |
| A2 | 1 | 0.0532 | No catalyst | 545 | 1000 | 107. | - |
| A3 | 1 | 0.0524 | 8.15 | 526 | 1000 | 27.2 | 72.8 |
| A4 | 1 | 0.0589 | 6.02 | 512 | 1000 | 10.9 | 89.1 |
| A5 | 1 | 0.0562 | 6.72 | 505 | 1000 | 76.8 | 23.2 |
| A6 | 1 | 0.0513 | 7.99 | 527 | 1000 | 13.4 | 86.6 |
| A7 | 1 | 0.0615 | 6.11 | 519 | 1000 | 14.0 | 86.0 |
| A8 | 1 | 0.0560 | 8.62 | 500 | 1000 | 16.5 | 83.5 |
| A9 | 1 | 0.0587 | 6.81 | 573 | 1000 | 15.7 | 84.3 |
| A10 | 1 | 0.0576 | 7.55 | 498 | 1000 | 14.4 | 85.6 |

A = Anthracene

* Thermocouple suspected to have broken off during run giving a false reading. New tubes prepared for runs A2 to A10.

TABLE 12

Hydrogenation of Anthracene over Sulfided Co-Mo/Catalyst

| Expt. No. | Residence Time (sec) | Anthracene (m moles) | Catalyst/A ratio (Wt/Wt) | Reaction Temp. $^{o}C$ | $PH_2$ (psig) | % Unreacted Anthracene | % Total Reaction Yield |
|---|---|---|---|---|---|---|---|
| A11 | 1 | o.o593 | 7.46(CoMo) | 482 | 1000 | 16.4 | 83.6 |
| A12 | 1 | 0.0553 | 7.60(CoMo) | 491 | 1000 | 16.7 | 83.3 |

A = Anthracene

TABLE 13

Hydrogenation of Naphthalene without catalyst

| Expt. No. | Residence Time (Sec) | Naphthalene (in mmoles) | Catalyst/N ratio (wt/wt) | Reaction Temp. $^{o}C$ | $PH_2$ (psi) | % Unreacted Naphthalene | % Total Reaction Yield |
|---|---|---|---|---|---|---|---|
| N1 | 1 | 0.0892 | - | 500 | 1000 | 96.1 | - |
| N2 | 1 | 0.0870 | - | 508 | 1000 | 95.6 | - |

N = Naphthalene

TABLE 14

Hydrogenation of Naphthalene over Sulfided Ni-W/Catalyst

| Expt. No. | Residence Time (sec) | Naphthalene (m moles) | Catalyst/N ratio (wt/wt) | Reaction Temp. $^{o}C$ | $PH_2$ (psig) | % Unreacted Naphthalene | % Total Reaction Yield |
|---|---|---|---|---|---|---|---|
| N3 | 1 | 0.0882 | 7.48 | 488 | 1000 | 61.0 | 39.0 |
| N4 | 1 | 0.0707 | 8.73 | 950* (Over heated) | 1000 | 0.57 | 99.43* |
| N5 | 1 | 0.0765 | 7.14 | 485 | 1000 | 66.0 | 34.0 |
| N6 | 1 | 0.0727 | 9.34 | 522 | 1000 | 54.9 | 45.1 |
| N7 | 1 | 0.0954 | 5.91 | 522 | 1000 | 68.3 | 31.7 |
| N9 | 1 | 0.0861 | 7.79 | 565 | 1000 | 68.4 | 31.6 |

N = Naphthalene

*Tube accidently overheated to 950$^{o}C$ and observed yield at this temperature is very high.

TEMP1 180 183

A 31

3rd Run 43

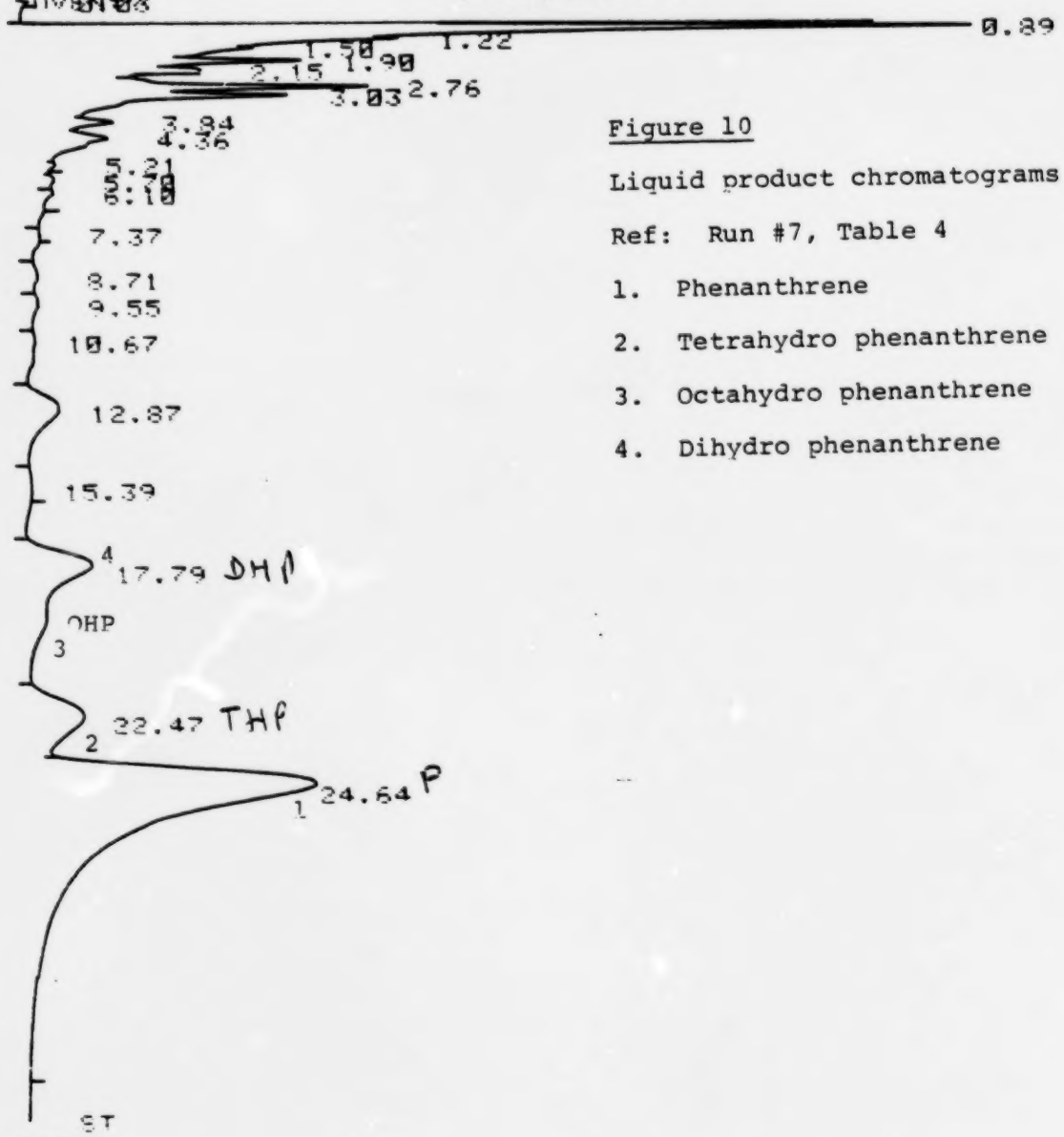



Figure 10

Liquid product chromatograms

Ref: Run #7, Table 4

1. Phenanthrene
2. Tetrahydro phenanthrene
3. Octahydro phenanthrene
4. Dihydro phenanthrene

| RTIME | AREA | AR% |
|---|---|---|
| 0.03 | 604 | 0.04 |
| 0.89 | 271900 | 16.73 |
| 1.22 | 82540 | 5.08 |
| 1.50 | 66160 | 4.07 |
| 1.90 | 55720 | 3.43 |
| 2.15 | 52540 | 3.23 |
| 2.76 | 87980 | 5.41 |
| 3.03 | 87820 | 5.40 |

3ul 7/ppm DHP

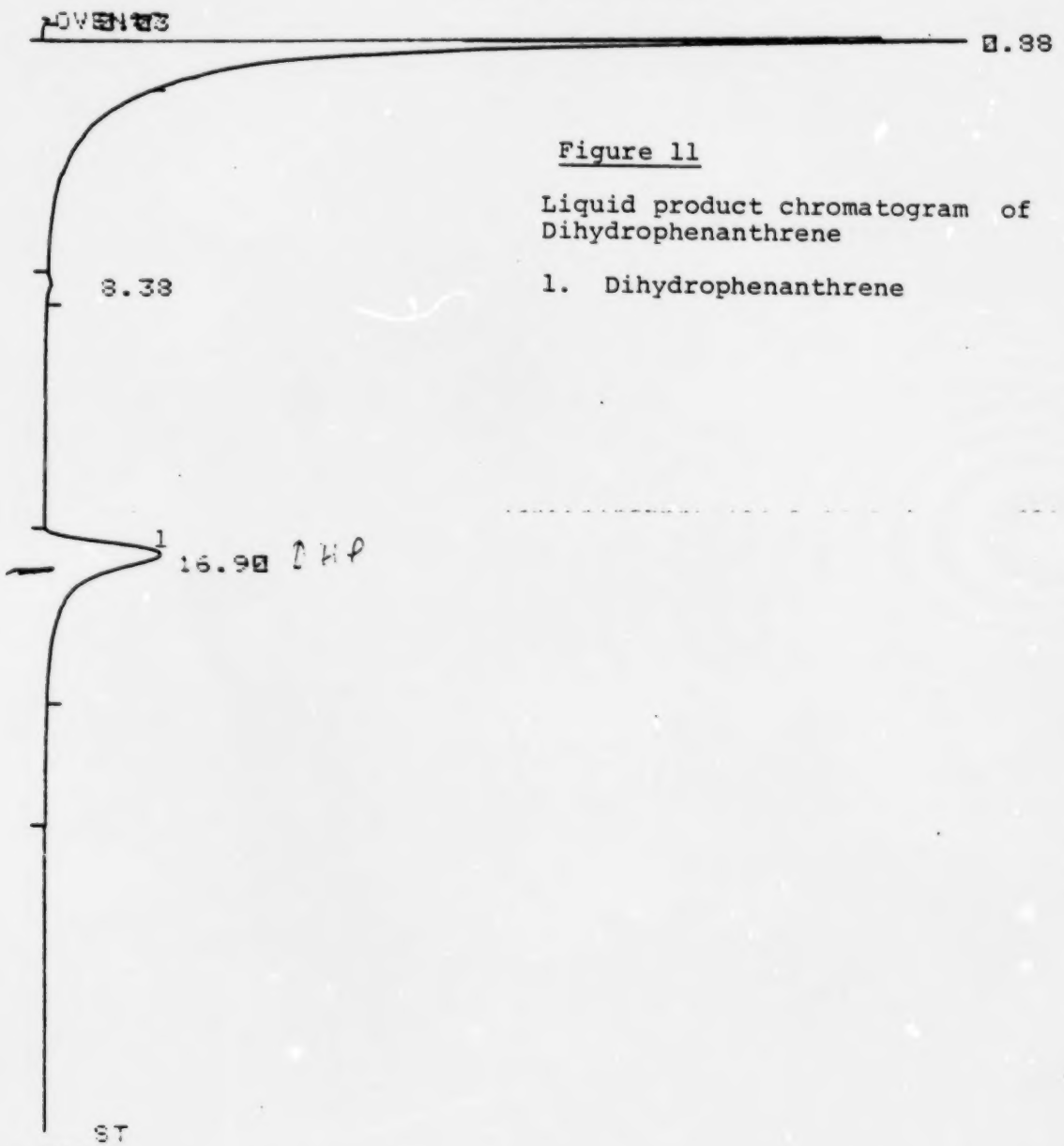



Figure 11

Liquid product chromatogram of Dihydrophenanthrene

1. Dihydrophenanthrene

ST

5830A

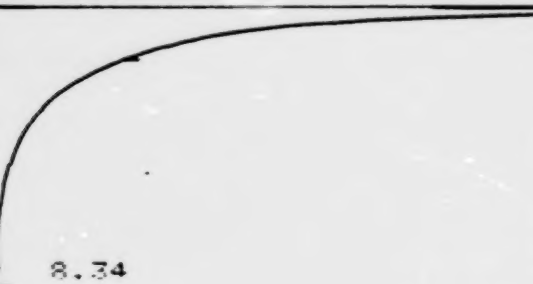
| RTIME | AREA | AR% |
|---|---|---|
| 0.03 | 598 | 0.11 |
| 0.88 | 388800 | 71.71 |
| 8.38 | 1992 | 0.37 |
| 16.90 | 150800 | 27.81 |

STOP
830A

| ME | AREA | AR% |
|---|---|---|
| 03 | 649 | 0.16 |
| 87 | 395300 | 99.33 |
| 34 | 2028 | 0.51 |

3ul Fresh $CS_2$

8.87



8.34

Figure 12

Chromatogram of the solvent, carbon disulfide

22.05

ST
830A

| ME | AREA | AR% |
|---|---|---|

3ul Run 45

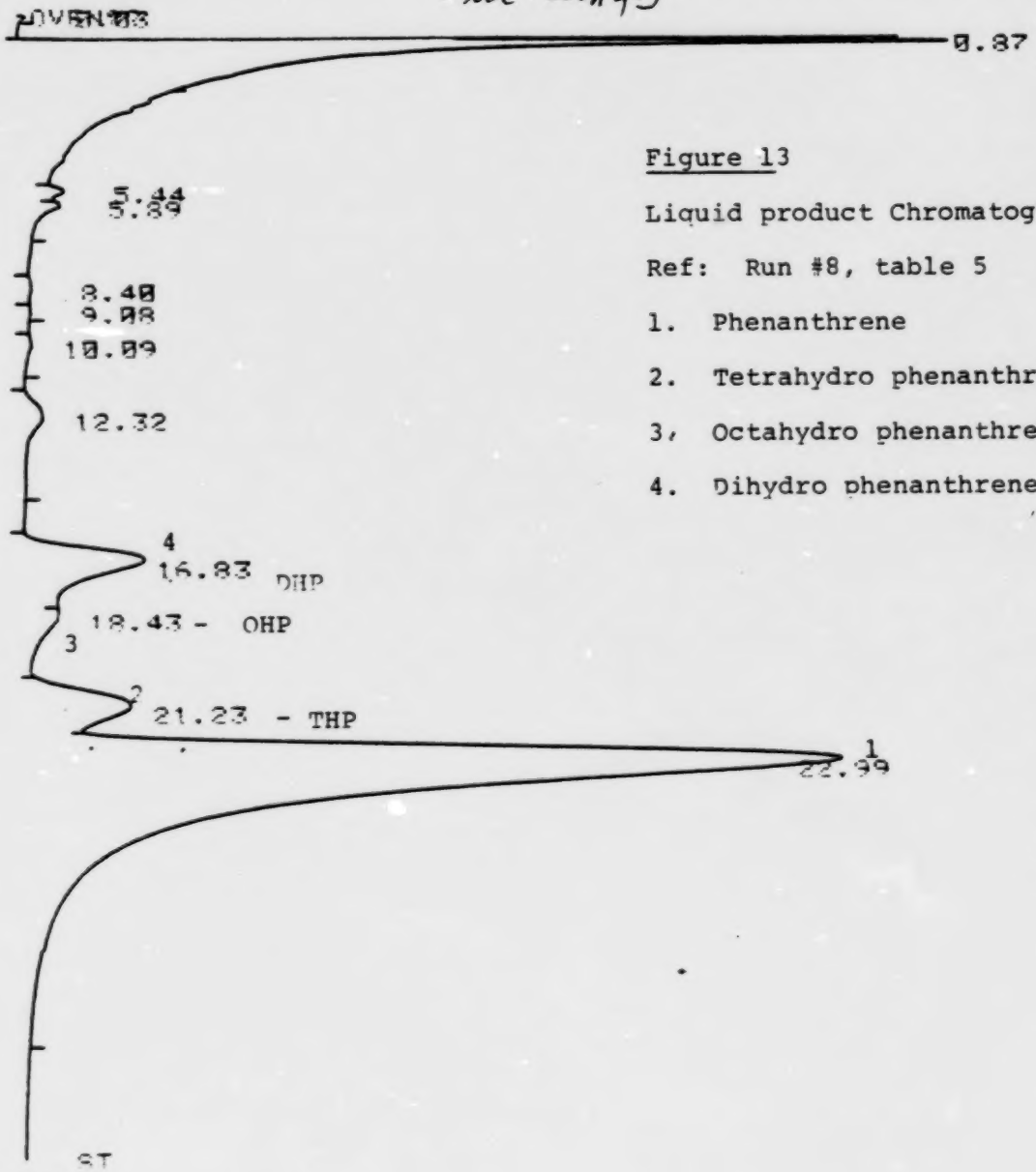



Figure 13

Liquid product Chromatograms

Ref: Run #8, table 5

1. Phenanthrene
2. Tetrahydro phenanthrene
3. Octahydro phenanthrene
4. Dihydro phenanthrene

ST

| RTIME | AREA | AR% |
|---|---|---|
| 0.03 | 699 | 0.03 |
| 0.87 | 402100 | 18.66 |
| 5.44 | 5473 | 0.25 |
| 5.89 | 6235 | 0.29 |
| 8.40 | 1348 | 0.06 |
| 9.08 | 624 | 0.03 |
| 10.09 | 2421 | 0.11 |
| 12.32 | 20598 | 0.96 |
| 16.83 | 131200 | 6.09 |
| 18.43 | 41498 | 1.93 |
| 21.23 | 120700 | 5.60 |
| 22.99 | 422000 | 65.99 |

3rd Run 46

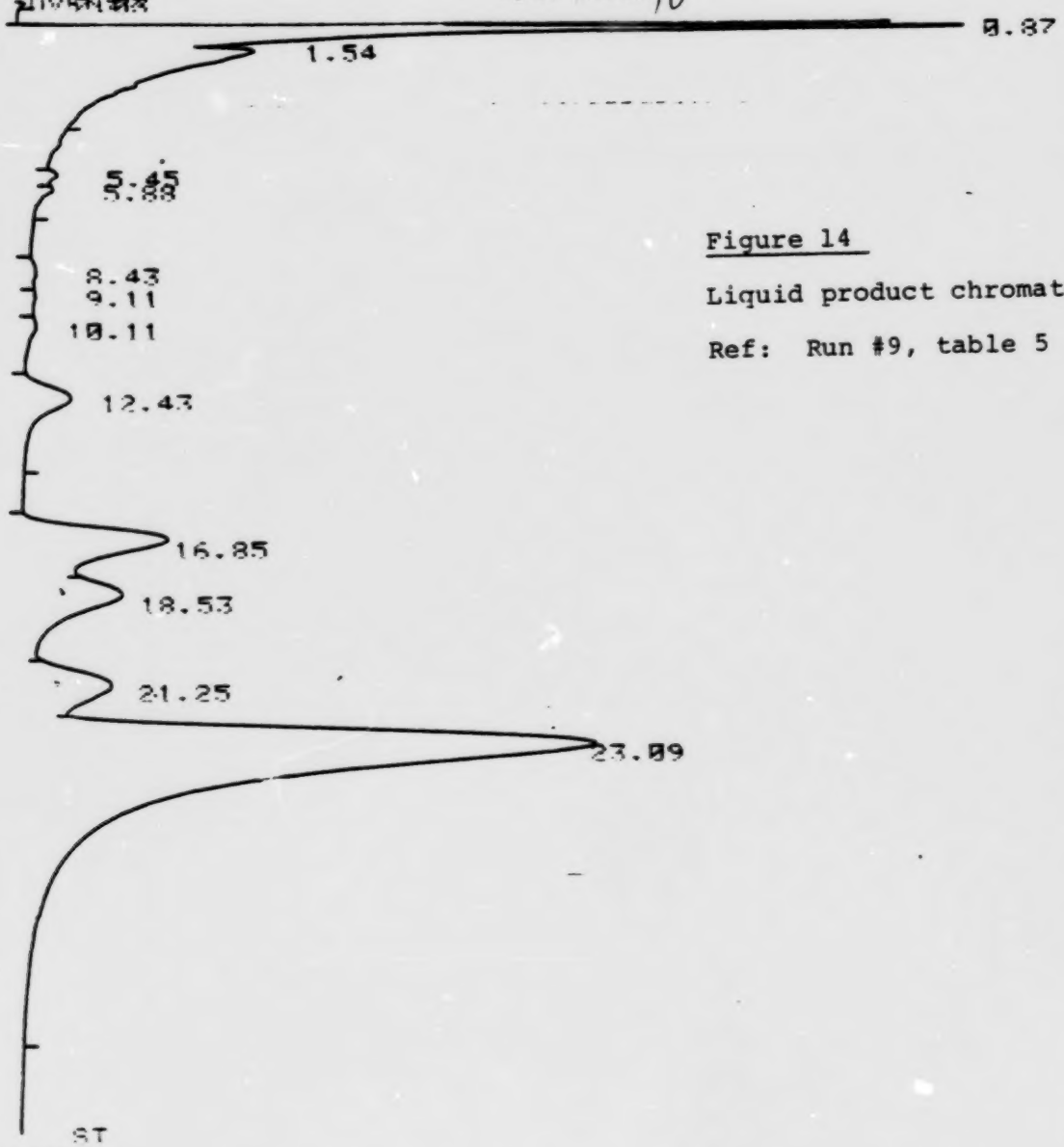



Figure 14

Liquid product chromatograms

Ref: Run #9, table 5

ST
he 5833A

| RTIME | AREA | AR% |
|---|---|---|
| 0.83 | 746 | 0.04 |
| 0.87 | 304900 | 14.82 |
| 1.54 | 242100 | 11.77 |
| 5.45 | 3741 | 0.18 |
| 5.88 | 3777 | 0.18 |
| 8.43 | 4239 | 0.21 |
| 9.11 | 5305 | 0.26 |
| 10.11 | 7432 | 0.36 |
| 12.43 | 47040 | 2.29 |
| 16.85 | 147900 | 7.19 |
| 18.53 | 134200 | 6.52 |
| 21.25 | 109700 | 5.33 |
| 23.09 | 1046000 | 50.85 |

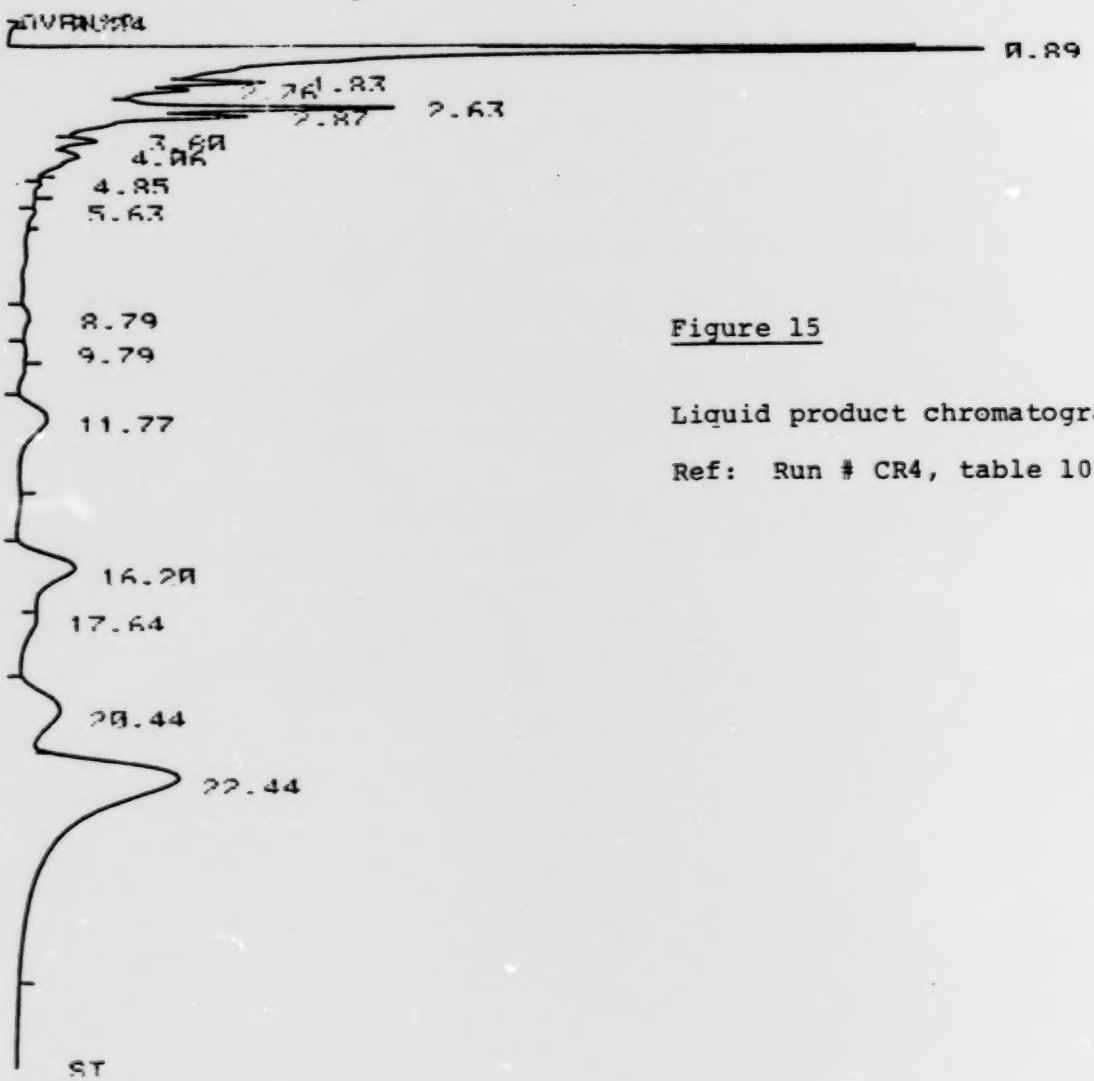



Figure 15

Liquid product chromatograms

Ref: Run # CR4, table 10

| RTIME | AREA | AR% |
|---|---|---|
| 0.84 | 984 | 0.09 |
| 0.89 | 378000 | 33.20 |
| 1.83 | 48610 | 4.27 |
| 2.06 | 46160 | 4.05 |
| 2.63 | 87080 | 7.65 |
| 2.87 | 69460 | 6.10 |
| 3.68 | 18990 | 1.67 |
| 4.06 | 21300 | 1.87 |
| 4.85 | 548 | 0.05 |
| 5.63 | 724 | 0.06 |
| 8.79 | 3889 | 0.34 |
| 9.79 | 1100 | 0.10 |
| 11.77 | 27240 | 2.39 |
| 16.28 | 62790 | 5.52 |
| 17.64 | 21520 | 1.89 |
| 20.44 | 55790 | 4.90 |
| 22.44 | 294200 | 25.84 |

| | |
|---|---|
| Oven Temp. | 180°C |
| Inj. Temp. | 270°C |
| Fid. Temp. | 270°C |
| Attn. | 128 |
| $N_2$ Flow | 31 |
| Column | 6ft. x 1/4" 5%SE30 on ChromP A/W 60-80 mesh |

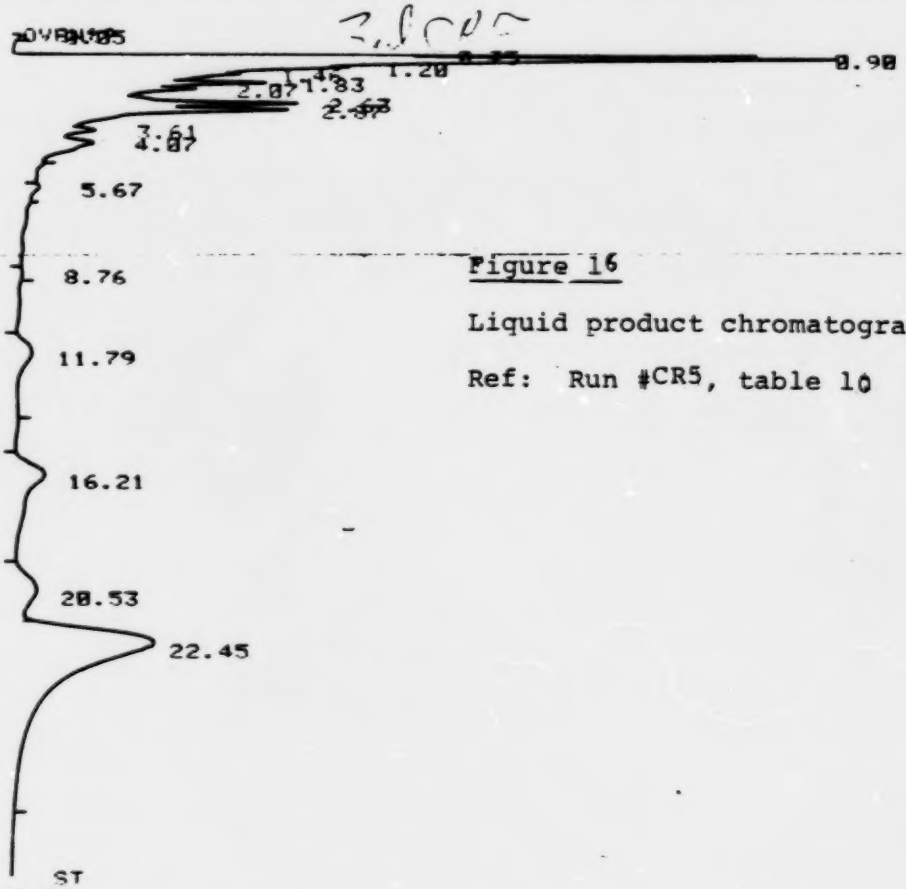



Figure 16

Liquid product chromatograms

Ref: Run #CR5, table 10

155

ST

| RTIME | AREA | AR% |
|---|---|---|
| 0.85 | 1171 | 0.10 |
| 0.75 | 17670 | 1.46 |
| 0.90 | 248200 | 20.57 |
| 1.20 | 30560 | 2.68 |
| 1.46 | 74320 | 6.16 |
| 1.83 | 61150 | 5.07 |
| 2.07 | 56680 | 4.70 |
| 2.63 | 89060 | 7.38 |
| 2.87 | 99240 | 8.22 |
| 3.61 | 22950 | 1.90 |
| 4.07 | 32310 | 2.68 |
| 5.67 | 1540 | 0.13 |
| 8.76 | 875 | 0.07 |
| 11.79 | 18950 | 1.57 |
| 16.21 | 50780 | 4.21 |
| 20.53 | 34940 | 2.90 |
| 22.45 | 316200 | 26.21 |

| | |
|---|---|
| Oven Temp. | 180°C |
| Inj. Temp. | 270°C |
| Fid. Temp. | 270°C |
| Attn. | 128 |
| $N_2$ Flow | 31 |
| Column | 6ft. x 1/4" |
| | 5%SE30 on ChromP A/W - 60-80 mesh |

23.53 1595000 78.84

Bed Run #3

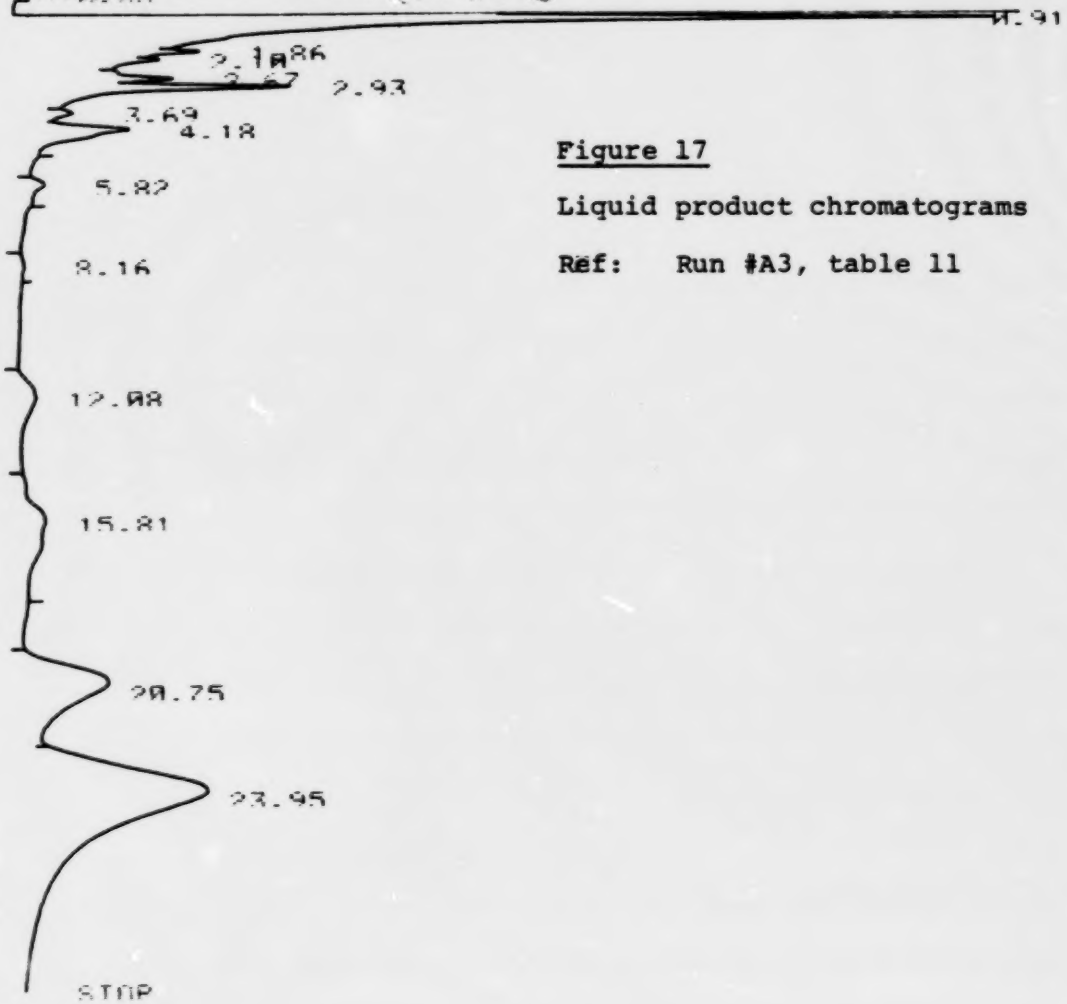



**Figure 17**

**Liquid product chromatograms**

**Ref: Run #A3, table 11**

| RETIME | AREA | AR% |
|---|---|---|
| 0.85 | 1991 | 0.16 |
| 2.91 | 384000 | 31.10 |
| 3.66 | 39440 | 3.19 |
| 4.18 | 41220 | 3.33 |
| 5.67 | 46400 | 3.76 |
| 8.43 | 77000 | 6.23 |
| 12.59 | 14260 | 1.07 |
| 15.18 | 40020 | 3.24 |
| 20.82 | 5467 | 0.44 |
| 23.16 | 1351 | 0.11 |
| 12.08 | 17790 | 1.44 |
| 15.81 | 35120 | 2.84 |
| 20.75 | 120300 | 9.73 |
| 23.95 | 412000 | 33.38 |

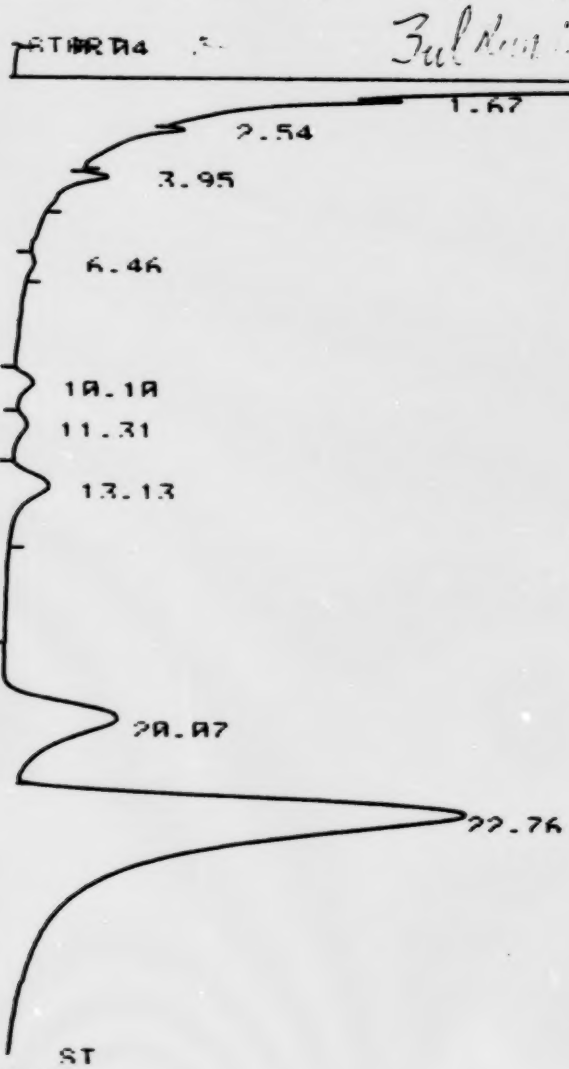



Figure 18

Liquid product chromatograms

Ref: Run # N6, table 14

| RTIME | AREA | AR% |
|---|---|---|
| 1.05 | 103300 | 6.00 |
| 1.23 | 341200 | 19.83 |
| 1.67 | 166600 | 9.68 |
| 2.54 | 64860 | 3.77 |
| 3.95 | 5920 | 0.34 |
| 6.46 | 2856 | 0.17 |
| 10.10 | 11890 | 0.69 |
| 11.31 | 11030 | 0.64 |
| 13.13 | 35690 | 2.07 |
| 20.07 | 146400 | 8.51 |
| 22.76 | 831000 | 48.29 |

| | |
|---|---|
| Oven Temp. | 110°C |
| Inj. Temp. | 270°C |
| Fid. Temp. | 270°C |
| Attn. | 128 |
| $N_2$ Flow | 31 |
| Column | 6ft. x 1/4" 5%SE30 on ChromP A/W 60-80 mesh |

In quantitative analysis of THP and OHP it was tacitly assumed that their FID response are similar to dihydrophenanthrene, which may not be correct.

FHP Products by GC/Mass

A sample in carbon disulfide solution of one of the phenanthrene hydropyrolysis reaction mixtures (ref: run #CR5, table 10) done at 500°C with sulfided nickel-tungsten on a alumina as catalyst was analyzed by G.C/M.S. Forty G.C. peaks were detected with an SE30 capillary column, 24 mass spectra were obtained and 6 mass chromatograms done. Tables 15, 16, 17, and 18 give tentative identifications of the products obtained in accordance with GC/Mass spectra of selected products shown in Fugures 19 to 25.

In many cases, for example spectrum #30, there are several possible isomers which give an identical or nearly identical mass spectrum. In these cases, other techniques such as IR., N.M.R. or U.V. spectrophotometry or the use of model compounds would be required for a positive identification. In other cases, several G.C. peaks gave mass spectra with the same m/e ratio for the molecualr ion and similar fragmentation patterns, for example spectra #34, 36 and 42 and the spectra #64 and 68 which are substituted biphenyl derivatives.

The mass chromatogram at m/e 192 showed five peaks (two poorly resolved) one of which, at a retention time of

TABLE 15

Flash Hydropyrolysis Products by GC/Mass

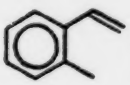
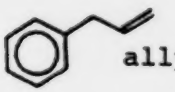
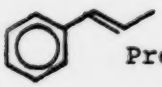
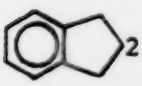
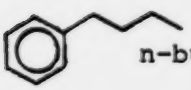
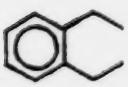
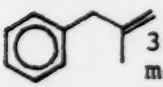
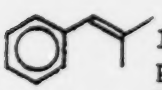
| Spectrum # | Retention Time (min) | Molecular Ion m/e | Identification (tentative) |
|---|---|---|---|
| 28 | 3.2 | 106 | $C_8H_{10}$; ethyl benzene |
| 30 | 4.8 | 118 | $C_9H_{10}$; may be  (O-Methylstyrene)  allylbenzene  Propenylbenzene  2,3-dihydroindene (Indan). |
| 32 | 4.9 | 134 | $C_{10H14}$ may be  n-butylbenzene or  1,2-diethylbenzene. |
| 34 | 5.3 | 132 | $C_{10}H_{12}$ may be  3-phenyl-2-methyl-prop-1-ene |
| 36 | 6.3 | 132 | $C_{10}H_{12}$ may be  1-phenyl-2-methyl prop-1-ene ( or vice-versa) |

Table 16
FHP products by GC/Mass



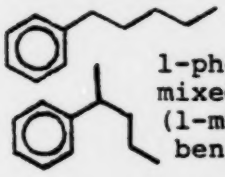
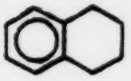
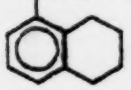
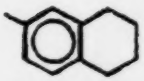
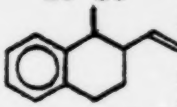
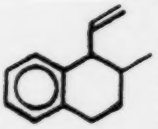
| Spectrum # | Rentention Time (min) | Molecular Ion m/e | Identification (Tentative) |
|---|---|---|---|
| 38 | 6.6 | 148 | $C_{11}H_{16}$ may be  1-phenylpentane mixed with (1-methylbutyl) benzene |
| 40 and | 6.8 | 132 | almost identical spectra (same G.C. peak |
| 42 | 6.9 | 132 | $C_{10}H_{12}$ may be  1,2,3,4,-tetrahydro naphthalene or one of the compounds listed under spectrum 34 or 36. |
| 44 | 7.3 | 128 | $C_{10}H_{8}$ Naphthalene |
| 46 | 9.1 | 146 | $C_{11}H_{14}$ may be  5-methyl-1,2,3,4,-tetrahydronaphthalene or  6- methyl-1,2,3,4,-tetrahydronaphthalene |
| 48 | 9.9 | 146 (197?) | Unknown (may be a fragment |
| 50 | 17.5 | 172 | $C_{13}H_{16}$ may be  1-methyl-2-vinyl-1,2,3,4,-tetrahydronaphthalene or  1-vinyl-2-methyl 1,2,3,4,-tetrahydro naphthalene or another $C_{13}H_{16}$ isomer. |

Table 17

FHP products by GC/Mass

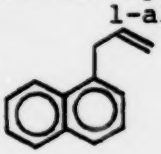
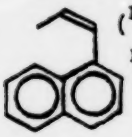
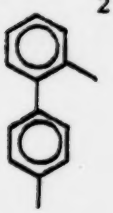
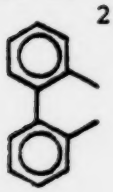
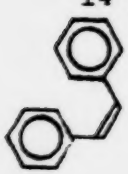
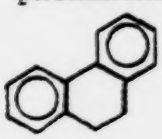
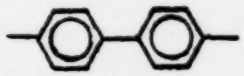
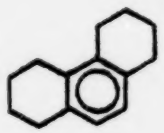
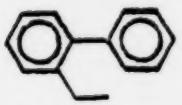
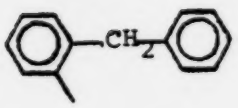
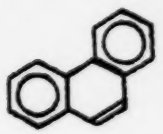
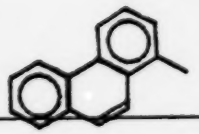
| Spectrum # | Retention Time (min) | Molecular Ion m/e | Identification Tentative) |
|---|---|---|---|
| 52 | 18.3 | 168 | $C_{13}H_{12}$ may be 1-allyl naphthalene  |
| 54 | 18.4 | 168 | $C_{13}H_{12}$ unknown isomer (maybe 1-propenyl-naphthalene)  |
| 56 | 19.5 | 182 | $C_{14}H_{14}$ 2,4' -dimethyl-biphenyl.  |
| 58 | 19.7 | 182 | $C_{14}H_{14}$ 2,2' -dimethyl-biphenyl  |
| 60 | 20.6 | 180 | $C_{14}H_{12}$ may be (cis) 1,2-diphenyl-ethene or more likely 9,10-dihydro-phenanthrene.   |
| 62 | 20.9 | 180 | $C_{14}H_{12}$ may be one of the isomers given for spectrum #60. |

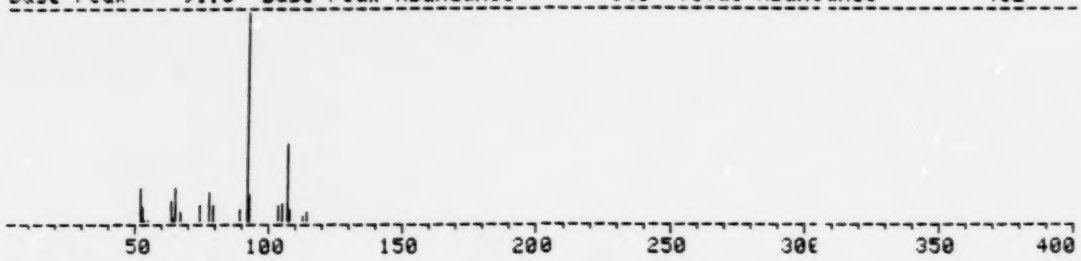
Table 18

FHP products by GC/Mass

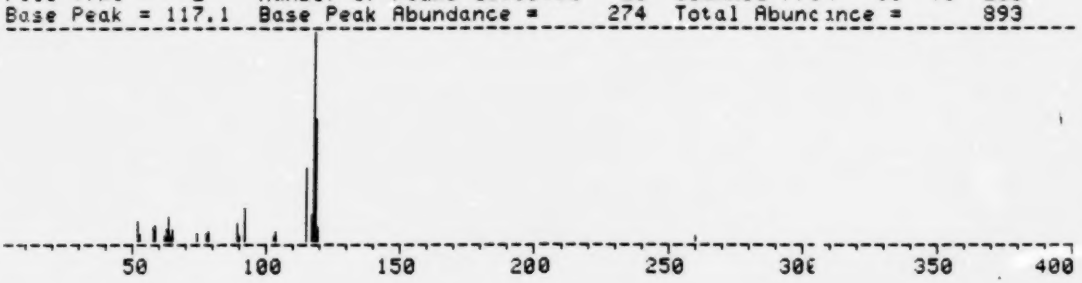
| Spectrum # | Retention Time (min) | Molecular Ion m/e | Identification Tentative) |
|---|---|---|---|
| 64 | 21.3 | 182 | $C_{14}H_{14}$ 4,4'-dimethyl-biphenyl  |
| 66 | 21.7 | 186 | $C_{14}H_{18}$ 1,2,3,4,5,6,7,8-octahydrophenanthrene.  |
| 68 | 22.4 | 182 | $C_{14}H_{14}$ may be 2- ethylbiphenyl  |
| 70 | 22.7 | 182 | $C_{14}H_{14}$ may be 2-methyldiphenyl-methane or another $C_{14}H_{14}$ isomer.   |
| 72 | 23.4 | 178 | $C_{14}H_{10}$ phenanthrene  |
| 74 | 26.5 | 192 | $C_{14}H_{24}$ may be 1-methylphenanthrene or the 2,3,4, or 9-methyl isomer.  |

Flexible Disk Spectrum Plot/Tab Program [Rev 79/03/09]

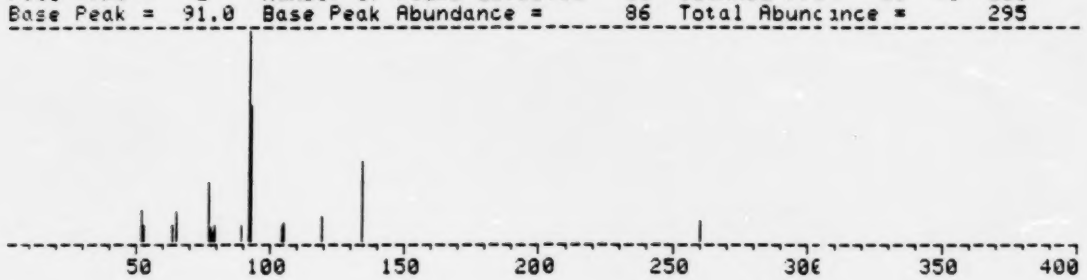
Spectrum # 28 Sample Identification # 3263 Retention Time (Min.) = 3.2
File type = 2 Number of peaks detected 20 Scanned from 51 to 114
Base Peak = 91.0 Base Peak Abundance = 146 Total Abundance = 402



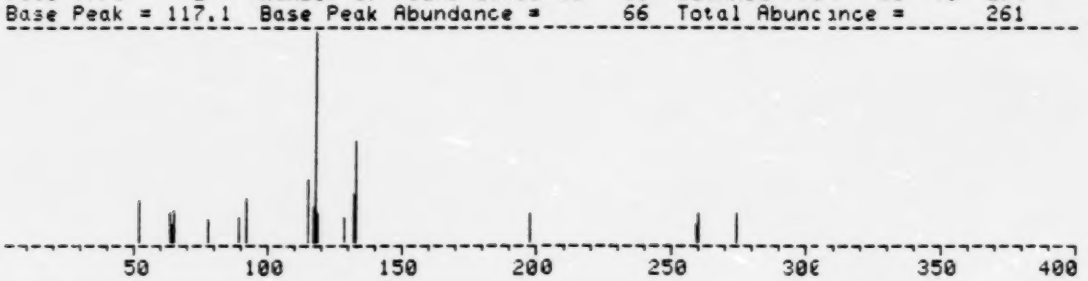

Spectrum # 30 Sample Identification # 3263 Retention Time (Min.) = 4.8
File type = 2 Number of peaks detected 23 Scanned from 51 to 260
Base Peak = 117.1 Base Peak Abundance = 274 Total Abundance = 893




Spectrum # 32 Sample Identification # 3263 Retention Time (Min.) = 4.9
File type = 2 Number of peaks detected 16 Scanned from 51 to 260
Base Peak = 91.0 Base Peak Abundance = 86 Total Abundance = 295




Spectrum # 34 Sample Identification # 3263 Retention Time (Min.) = 5.3
File type = 2 Number of peaks detected 18 Scanned from 51 to 274
Base Peak = 117.1 Base Peak Abundance = 66 Total Abundance = 261




Spectrum # 36 Sample Identification # 3263 Retention Time (Min.) = 6.3
File type = 2 Number of peaks detected 16 Scanned from 51 to 274
Base Peak = 117.0 Base Peak Abundance = 52 Total Abundance = 206

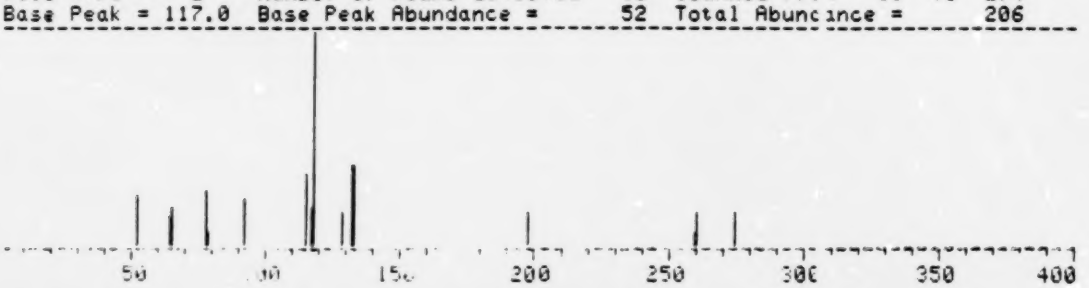



Figure 19

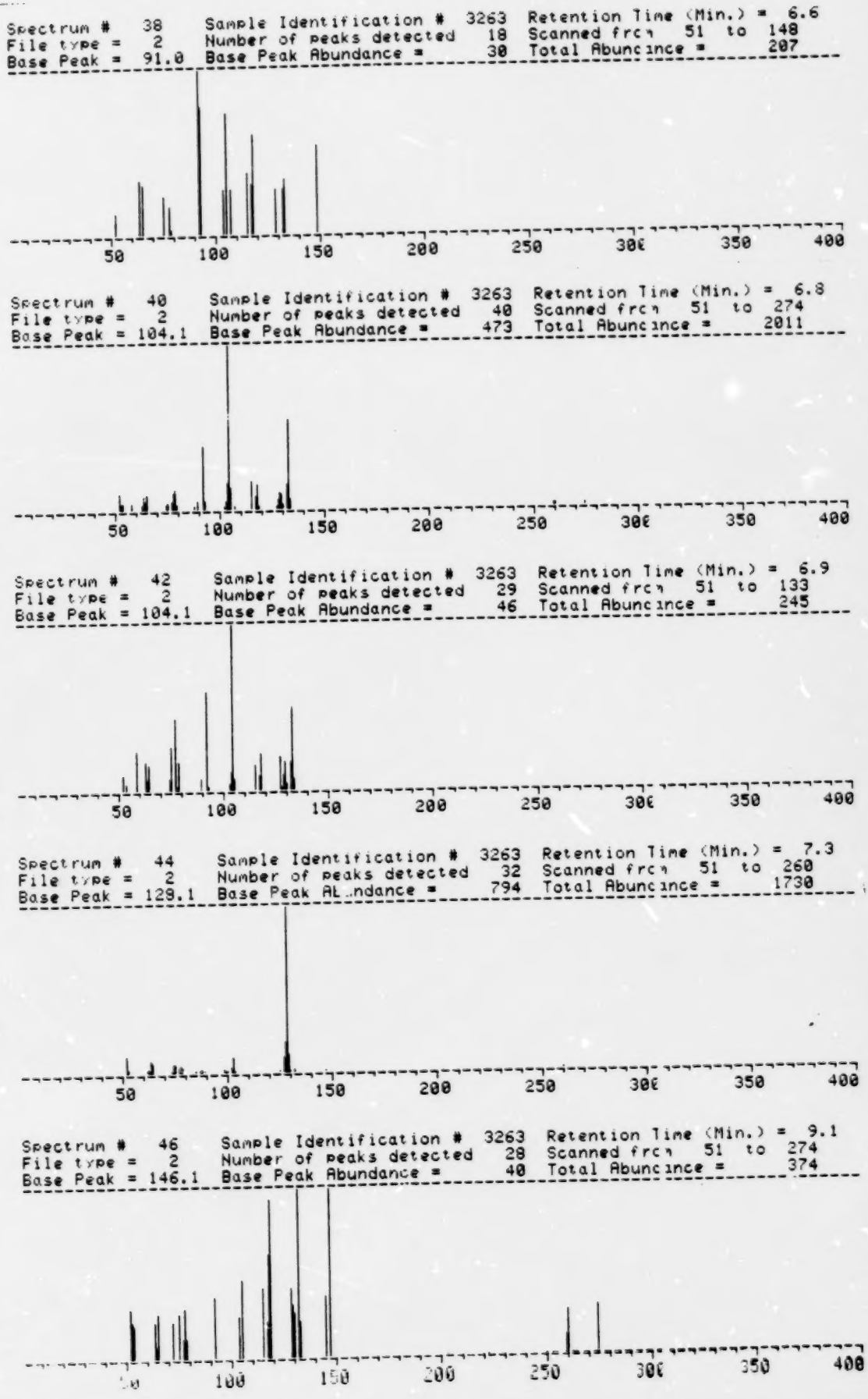

Spectrum # 38 Sample Identification # 3263 Retention Time (Min.) = 6.6
File type = 2 Number of peaks detected 18 Scanned from 51 to 148
Base Peak = 91.0 Base Peak Abundance = 30 Total Abundance = 207
50 100 150 200 250 300 350 400
Spectrum # 40 Sample Identification # 3263 Retention Time (Min.) = 6.8
File type = 2 Number of peaks detected 40 Scanned from 51 to 274
Base Peak = 104.1 Base Peak Abundance = 473 Total Abundance = 2011
50 100 150 200 250 300 350 400
Spectrum # 42 Sample Identification # 3263 Retention Time (Min.) = 6.9
File type = 2 Number of peaks detected 29 Scanned from 51 to 133
Base Peak = 104.1 Base Peak Abundance = 46 Total Abundance = 245
50 100 150 200 250 300 350 400
Spectrum # 44 Sample Identification # 3263 Retention Time (Min.) = 7.3
File type = 2 Number of peaks detected 32 Scanned from 51 to 260
Base Peak = 129.1 Base Peak Abundance = 794 Total Abundance = 1730
50 100 150 200 250 300 350 400
Spectrum # 46 Sample Identification # 3263 Retention Time (Min.) = 9.1
File type = 2 Number of peaks detected 28 Scanned from 51 to 274
Base Peak = 146.1 Base Peak Abundance = 40 Total Abundance = 374
50 100 150 200 250 300 350 400

Figure 20

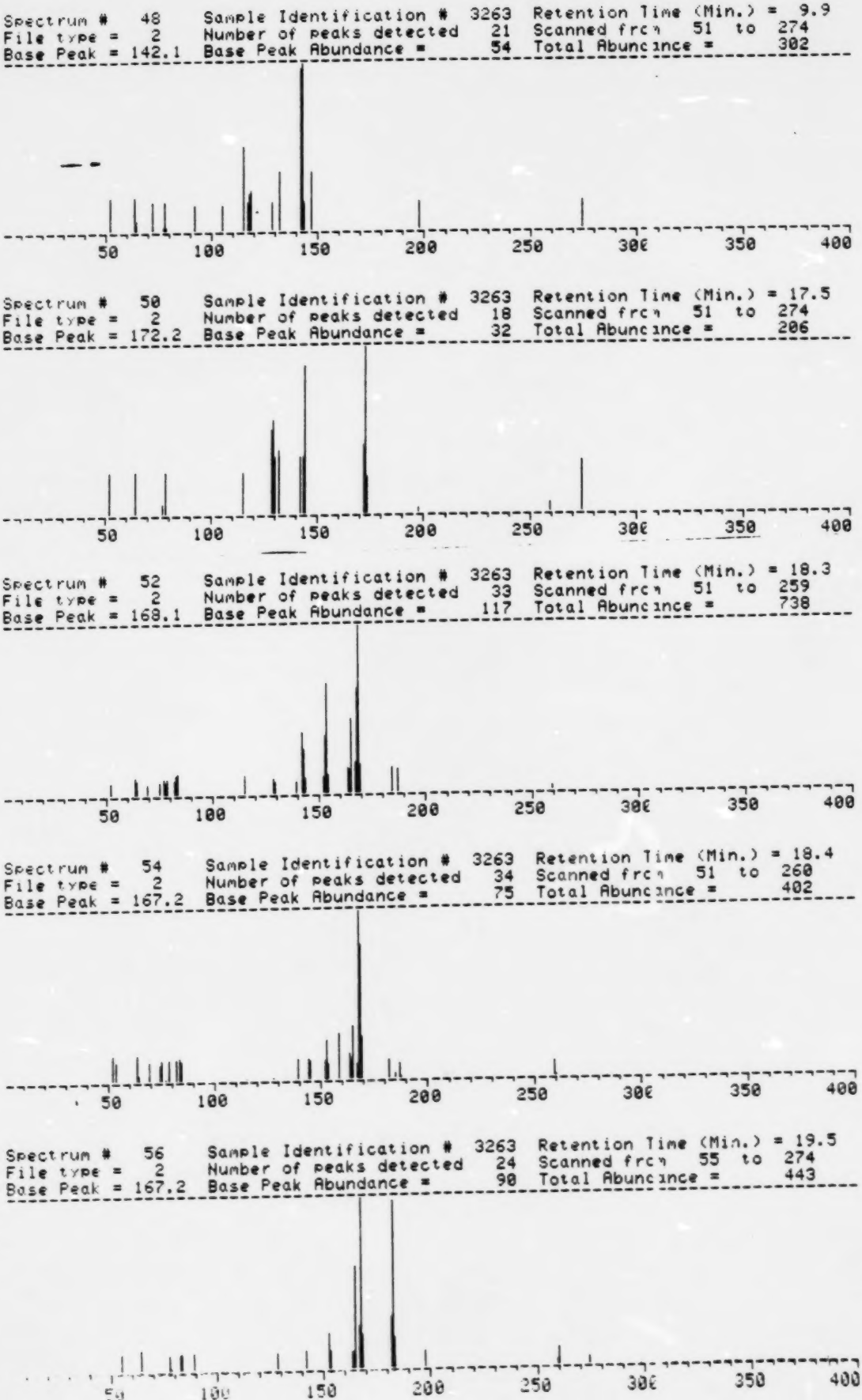

Spectrum # 48 Sample Identification # 3263 Retention Time (Min.) = 9.9
File type = 2 Number of peaks detected 21 Scanned from 51 to 274
Base Peak = 142.1 Base Peak Abundance = 54 Total Abundance = 302
50 100 150 200 250 300 350 400
Spectrum # 50 Sample Identification # 3263 Retention Time (Min.) = 17.5
File type = 2 Number of peaks detected 18 Scanned from 51 to 274
Base Peak = 172.2 Base Peak Abundance = 32 Total Abundance = 206
50 100 150 200 250 300 350 400
Spectrum # 52 Sample Identification # 3263 Retention Time (Min.) = 18.3
File type = 2 Number of peaks detected 33 Scanned from 51 to 259
Base Peak = 168.1 Base Peak Abundance = 117 Total Abundance = 738
50 100 150 200 250 300 350 400
Spectrum # 54 Sample Identification # 3263 Retention Time (Min.) = 18.4
File type = 2 Number of peaks detected 34 Scanned from 51 to 260
Base Peak = 167.2 Base Peak Abundance = 75 Total Abundance = 402
50 100 150 200 250 300 350 400
Spectrum # 56 Sample Identification # 3263 Retention Time (Min.) = 19.5
File type = 2 Number of peaks detected 24 Scanned from 55 to 274
Base Peak = 167.2 Base Peak Abundance = 90 Total Abundance = 443
50 100 150 200 250 300 350 400

Figure 21

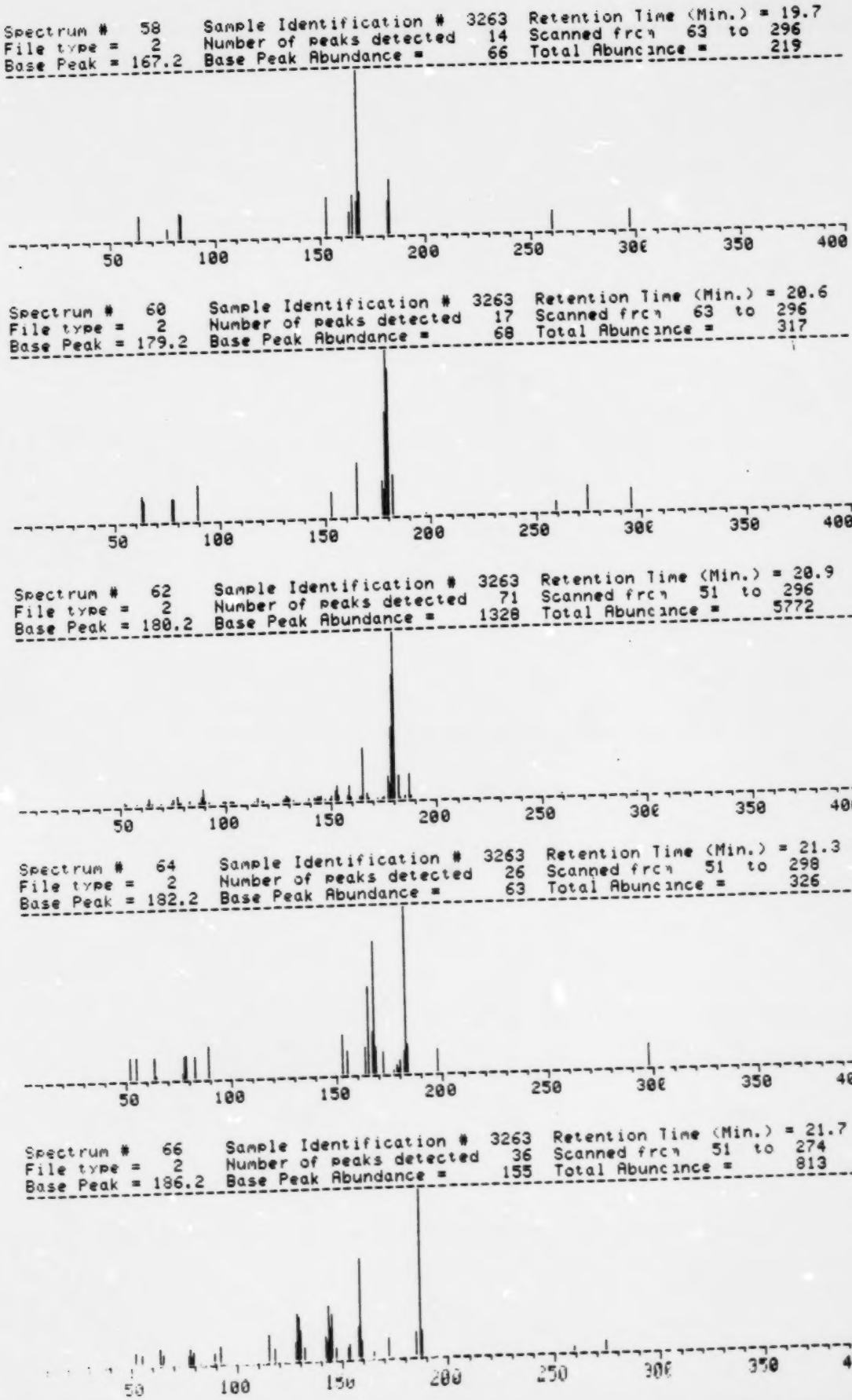

Spectrum # 58
File type = 2
Base Peak = 167.2
Sample Identification # 3263
Number of peaks detected 14
Base Peak Abundance = 66
Retention Time (Min.) = 19.7
Scanned from 63 to 296
Total Abundance = 219
50 100 150 200 250 300 350 400
Spectrum # 60
File type = 2
Base Peak = 179.2
Sample Identification # 3263
Number of peaks detected 17
Base Peak Abundance = 68
Retention Time (Min.) = 20.6
Scanned from 63 to 296
Total Abundance = 317
50 100 150 200 250 300 350 400
Spectrum # 62
File type = 2
Base Peak = 180.2
Sample Identification # 3263
Number of peaks detected 71
Base Peak Abundance = 1328
Retention Time (Min.) = 20.9
Scanned from 51 to 296
Total Abundance = 5772
50 100 150 200 250 300 350 400
Spectrum # 64
File type = 2
Base Peak = 182.2
Sample Identification # 3263
Number of peaks detected 26
Base Peak Abundance = 63
Retention Time (Min.) = 21.3
Scanned from 51 to 298
Total Abundance = 326
50 100 150 200 250 300 350 400
Spectrum # 66
File type = 2
Base Peak = 186.2
Sample Identification # 3263
Number of peaks detected 36
Base Peak Abundance = 155
Retention Time (Min.) = 21.7
Scanned from 51 to 274
Total Abundance = 813
50 100 150 200 250 300 350 400

Figure 22

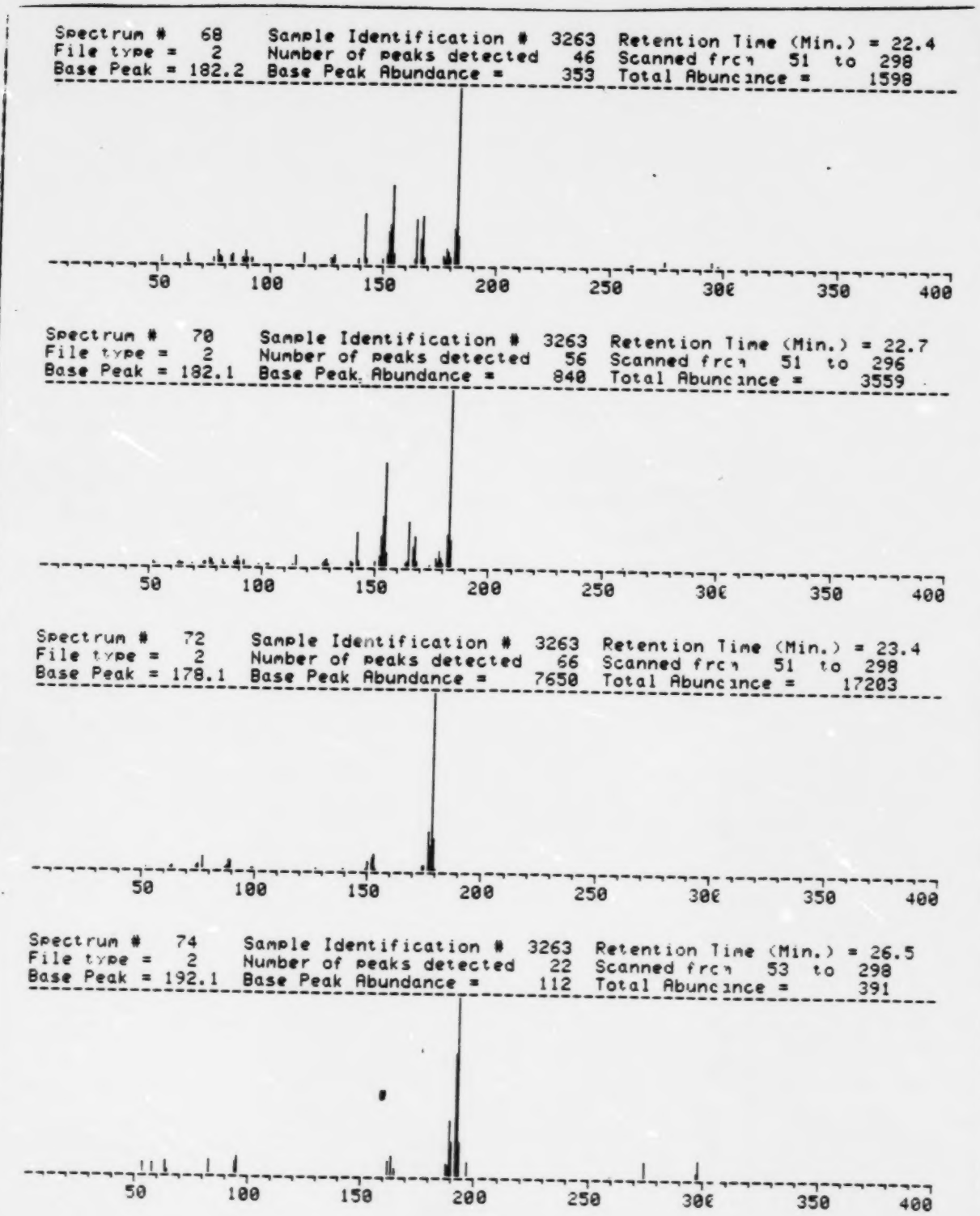

Spectrum # 68 Sample Identification # 3263 Retention Time (Min.) = 22.4
File type = 2 Number of peaks detected 46 Scanned from 51 to 298
Base Peak = 182.2 Base Peak Abundance = 353 Total Abundance = 1598
50 100 150 200 250 300 350 400
Spectrum # 70 Sample Identification # 3263 Retention Time (Min.) = 22.7
File type = 2 Number of peaks detected 56 Scanned from 51 to 296
Base Peak = 182.1 Base Peak Abundance = 840 Total Abundance = 3559
50 100 150 200 250 300 350 400
Spectrum # 72 Sample Identification # 3263 Retention Time (Min.) = 23.4
File type = 2 Number of peaks detected 66 Scanned from 51 to 298
Base Peak = 178.1 Base Peak Abundance = 7650 Total Abundance = 17203
50 100 150 200 250 300 350 400
Spectrum # 74 Sample Identification # 3263 Retention Time (Min.) = 26.5
File type = 2 Number of peaks detected 22 Scanned from 53 to 298
Base Peak = 192.1 Base Peak Abundance = 112 Total Abundance = 391
50 100 150 200 250 300 350 400

Figure 23

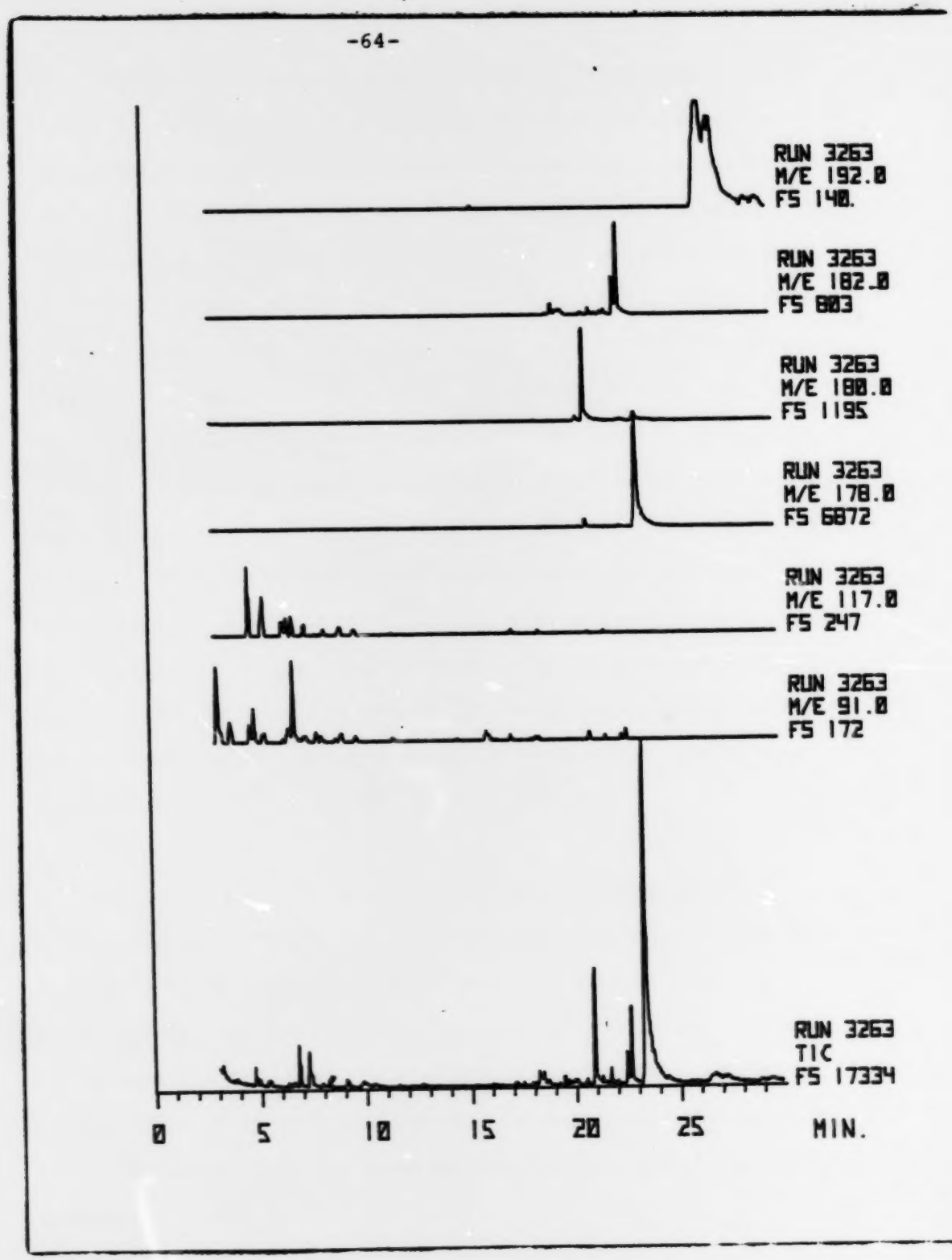
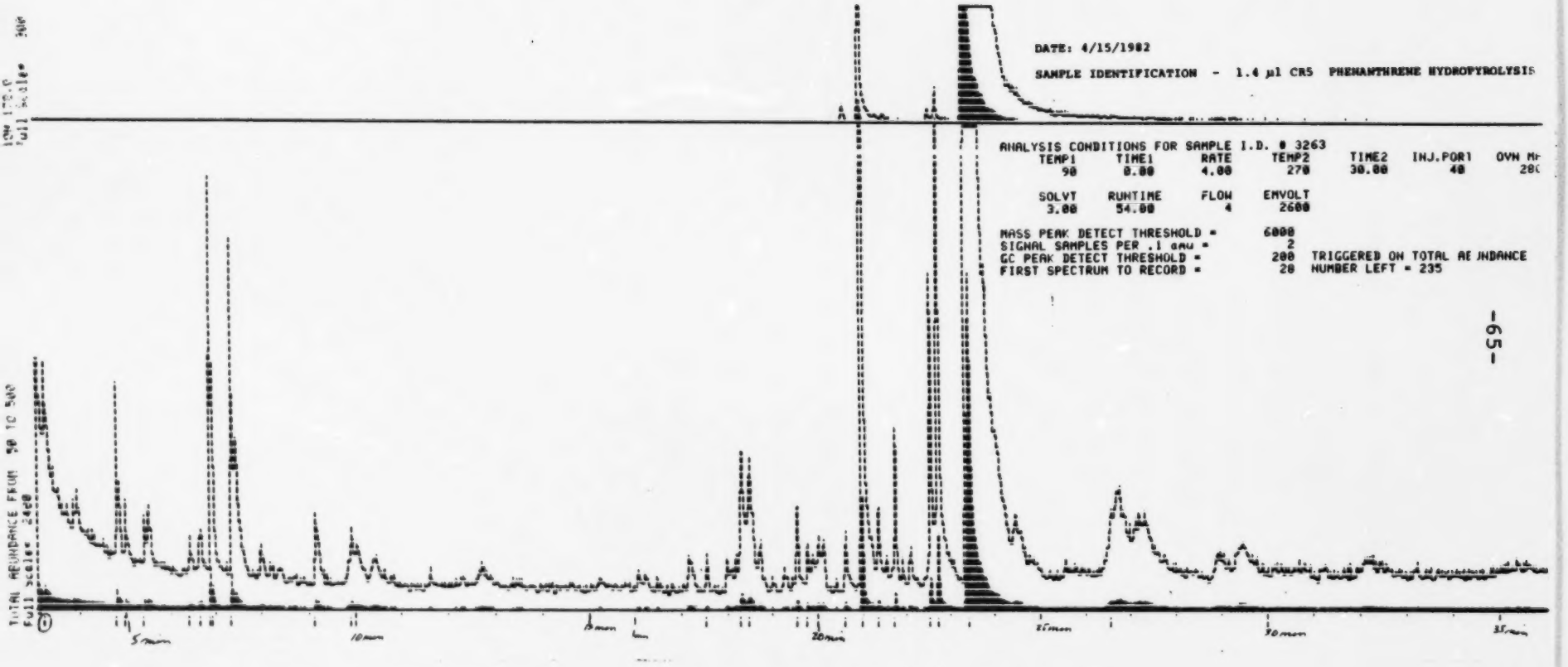

RUN 3263
M/E 192.0
FS 140.
RUN 3263
M/E 182.0
FS 803
RUN 3263
M/E 180.0
FS 1195
RUN 3263
M/E 178.0
FS 6872
RUN 3263
M/E 117.0
FS 247
RUN 3263
M/E 91.0
FS 172
RUN 3263
TIC
FS 17334
0
5
10
15
20
25
MIN.

Figure 24

Figure 25


DATE: 4/15/1982
SAMPLE IDENTIFICATION - 1.4 µl CR5 PHENANTHRENE HYDROPYROLYSIS
ANALYSIS CONDITIONS FOR SAMPLE I.D. # 3263
TEMP1 TIME1 RATE TEMP2 TIME2 INJ.PORT OVN M
90 0.00 4.00 270 30.00 40 28
SOLVT RUNTIME FLOW EMVOLT
3.00 54.00 4 2600
MASS PEAK DETECT THRESHOLD = 6000
SIGNAL SAMPLES PER .1 amu = 2
GC PEAK DETECT THRESHOLD = 200 TRIGGERED ON TOTAL ABUNDANCE
FIRST SPECTRUM TO RECORD = 28 NUMBER LEFT = 235
TOTAL ABUNDANCE FROM 50 TO 500
Full Scale= 2400
5min
10min
15min
20min
25min
30min
35min

26.5 minutes, was found to be a methylphenanthrene isomer. Since the five possible methylphenanthrene isomers have virtually indistinguishable mass spectra, it is likely that the other four peals consist of the other four isomers. The use of authentic model compounds would be required to determine when each isomer elutes. It is likely that the methylphenanthrene isomers were present as impurities in the phenanthrene starting material.

The mass chromatogram at m/e 182 shows two major peaks at retention times of 22.7 and 22.4 minutes which could be tetrahydrophenanthrene but appear from the mass spectra to be more likely biphenayl or diphenylmethane derivatives. Minor peaks at retention times of 21.3, 19.7 and19.5 minutes are almost certainly biphenyl derivatives. Again, the use of model compounds and other spectroscopic techniques could clarify the identity of the isomers.

The m/e 180 peak at a retention time of 20.9 minutes is most likely 9, 10-dihydrophenanthrene although diphenylethene cannot be ruled out. A smaller peak at a retention time of 20.6 minutes may be the latter isomer. Trace amounts of eight other isomers appear to be present in the m/e 180 mass chromatogram. Model compounds would be required for a more positive identification based on their retention time.

Further mass chromatograms will be required at m/e 114, 118, 128, 132, 134, 146, 148, 172,184, 186, 188 and 190 to aid in the identification of other hydropyrolysis product isomers. Mass spectra should also be done on additional G.C. peaks, particualarly those at retention times less than 3.2 minutes. G.C./M.S. analyses should also be done on gaseous products in the near future.

Gaseous Products

A single attempt to collect gaseous products by cooling the trap with liquid nitrogen instead of dry ice followed by a warming of the trap to room temperature while flushing it with nitrogen into a gas sampling bag was unsuccessful. Samples were taken by syringe from the gas sampling bag and injected into the gas chromatograph. These samples may have been too dilute to be detected.

# VI DISCUSSION

The complexity of the spectrum is evident upon inspection of the chromatograms of figures 10 to 18 and GC/Mass, figures 19 to 25 used for the product identification.

The yields are similar for both catalysts, Ni-W and Co-Mo. The average conversion for thirty phenanthrene runs was found to be about 82%. The average conversion for nine anthracene runs was found to be about 84%. However, in case of naphthalene the average reaction yield was only about 36%. These observations and the product formation appear to support the view that hydrogenation reactions generally take place in a stepwise fashion. The first hydrogenation product of phenanthrene is 9, 10 di-hydro-phenanthrene. Further hydrogenation produces successively the tetrahydro, octahydro and perhydro products. Anthracene and naphthalene are hydrogenated same way.

From the type of the products that are observed in this investigation suggest free radical hydrogenolysis of polynuclear aromatic ring of Penninger and Slotboom (22). In addition to terminal ring cleavage the observed products such as ethylbiphenyl may be due to cracking at the central ring. The conversion to cracked products could not be quantitatively identified.

The observation that the yield of naphthalene hydro-genation is low under similar experimental conditions supports

the view that the ease of hydrogenation tends to increase with increasing size of the molecule. The relative rates of hydrogenation of benzene, naphthalene and anthracene over a tungsten sulfide catalyst have been reported in the literature as 100, 2300 and 6187.

The catalyst chosen for this investigation is Ni-W and Co-Mo. Both the catalysts were presulfided so that the active form of the catalysts contained Ni-W and Co-Mo as sulfide. Modern commercial hydroconversion processes generally utilize sulfur and nitrogen resistant catalysts.

Both the catalysts used in FHP experiments are of considerable interest. First the catalysts have been found in this study to have high activity in hydrogenation and conversion reactions of phenanthrene and anthracene. In addition the conversion to lower molecular weight species has been obtained.

## VII SUGGESTION FOR FURTHER WORK

In view of the very promising results of this study the project should be continued.

A detailed proposal has been submitted to Energy Mones and Resources, Ottawa for consideration of the following work:

(1) Quantitative Analysis of major reaction products including gases should be undertaken to obtain approximate material balance on carbon.

The following possible products varying from $C_1$ to $C_{14}$ should be analyzed from the retention times of pure compounds and from GC-Mass spectrometry.

| Formula | Name | Method of Analysis Retentime* | GC/ms |
|---|---|---|---|
| $CH_4$ | Methane | | X |
| $C_2H_6$ | Ethane | | X |
| $C_3H_8$ | Propane | | X |
| $C_4H_{10}$ | Isobutane | | X |
| $C_4H_{10}$ | Butane | | X |
| $C_5H_{10}$ | Cyclopentane | | X |
| $C_6H_{14}$ | 2-Methylpentane | | X |
| $C_6H_{14}$ | n-Hexane | | X |

| Formula | Name | Method of Analysis Retentime* | GC/ms |
|---|---|---|---|
| $C_6H_6$ | Benzene | X | |
| $C_7H_8$ | Toluene | X | |
| $C_8H_{10}$ | Ethylbenzene | X | |
| $C_8H_{10}$ | Xylene | X | |
| $C_{10}H_{14}$ | n-Butylbenzene | X | |
| $C_{10}H_{18}$ | Decalin | X | |
| $C_{11}H_{16}$ | Methyl-butylbenzene | | |
| $C_{10}H_{12}$ | Tetralin | X | X |
| $C_{10}H_{18}$ | Naphthalene | X | |
| $C_{11}H_{10}$ | 2-Methylnaphthalene | | |
| $C_{12}H_{16}$ | Cyclohexylbenzene | | X |
| $C_{12}H_{16}$ | 1-Ethyltetralin | | |
| $C_{12}H_{10}$ | Biphenyl | X | X |
| $C_{14}H_{24}$ | Perhydrophenanthrenes | | X |
| $C_{14}H_{18}$ | Octahydrophenanthrene isomer | | X |
| $C_{14}H_{12}$ | Dihydrophenanthrene isomer | X | |
| $C_{14}H_{14}$ | Tetrahydrophenanthrene | | |
| $C_{14}H_{10}$ | Phenanthrene | X | X |

* Available form commercial sources:
New Aldrich catalogue and P & B.

(ii) To conduct Naphthalene runs at high severities particularly at higher temperature.

(iii) FHP experiments using the catalysts of this investigation should be extended to four and five membered rings, such as chrysene and Perylene respectively.

(lV) The poisoning effect of S, N and O containing species such as thiophene, carbazole and diphenylene oxide respectively should be studied. This study is considered essential for the evaluation and practical utility of the catalysts.

(V) Effect of organometallic compounds such as potassium salt of phenol and potassium salt of m-cresol should be studied to evaluate catalyst.

(VI) Catalyst to feed ratio should be varied to more ecomomical side.

(VII) Conversion should be optimized towards lower Hydrogen pressure for economy of the process.

(VIII) The practical utilization of catalysts in such large concentrations as used in this investigation would require the development of low cost and efficient catalyst separation, recovery and regeneration procedure for process development. Ideally, the catalysts should not be used in massive amounts for the hydrogenation and hydrocracking of polynuclear hydrocarbons. It is important that FHP experiments be carried out with catalyst to feed ratio less than unity. One interesting feature of Ni-W and Co-Mo as hydrocracking catalysts for polynuclear hydrocarbons is to be examined and that is their selectivity to products boiling in the gasoline range. The effect of catalyst/feed ration on the product distribution should be carefully studied.

Recent study* on chemical composition of Athabasca bitumen have identified the following compounds in various aromatics:

---

* Milan L. Selucky, Y. Chu, T. Ruo and Otto P. Strausz, Hydrocarbon Research Centre, University of Alberta, FUEL, October 1977, Vol 56, p 369-381.

Monoaromatics

Alkylbenzene,

Naphthalenebenzene and

Dinaphthenelbenzene

Diaromatics

Naphthalenes,

Acenaphthenes,

Dibenzofurans and

Fluorenes

Triaromatics

Phenanthrenes and

Naphthenphenanthrenes

Tetraaromatics

Pyrenes and chrysenes

Pentaaromatics

Perylenes and

Dibenzanthracenes

Thiopheno aromatics

Benzothiophenes

Dibenzothiophenes

Naphthobenzothiophenes.

The catalysts should therefore be evaluated for each class of aromatics i.e. mono to penta individually and then in the presence of poisons. The experimental conditions should therefore be optimized for both, high quality products and high conversion rates.

(IX) The optimum conditions selected from individual model compounds as above should then be applied to real Athabasca bitumen feed.

(X) It was beyond the scope of the present investigation to evaluate catalyst deactivation kinetics. It is necessary to study the decline in catalyst activity. To test for the deactivation of the catalyst a continuous flow reactor has been proposed with modification of the existing apparatus. It is also possible to recover and reuse the catalyst from the FHP apparatus in order to determine the extent of deactivation upon repeated use.
The use of the larger samples in a continuous flow system would also permit identification by other techniques such as IR, NMR, UV spectroscopy and CHNS analysis.

(XI) Based upon the success of the above studies a process should be developed and patent obtained.

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## APPENDIX

Unsuccessful Experiments for Attempted Hydrogenation of Phenanthrene with Formic Acid and its Salts in the Presence of Catalysts.

BY

G. Kruger, PhD., Sydney

## INTRODUCTION

In the work statement of this project it was proposed to study the conversion of phenanthrene to products by FHP technique, and also by hydrogen transfer from formic acid and the formate anion at temperature below 100°C and at atmospheric pressure. Though in general catalysts have not been employed in the FHP process we found large conversion and desirable products in their presence as has been presented in the text of this report. The catalytic system and technique developed for FHP have sufficient novelty and utility to obtain patent protection for it.

While the assembly of FHP apparatus was in progress the transfer of hydrogen from formic acid and its anion to phenanthrene experiments were attempted. This study was stimulated by previous unpublished work of Dr. G. Kruger.

G. Kruger found that formic acid in conjunction with an excess of t-butylamine and in presence of palladium can be used instead of hydrogne gas for the reduction of olefinic double bonds, such as present in the steriods progesterone, where an olfinic double bond is conjugated to a keto group, and ergosterol, which contains a homannular diene. With the catalyst formulations used no elevation of the tempertaure above room temperature and of the pressure above atmospheric pressure was necessary.

Unpublished work carried out by G. Kruger in 1962 and 1963 also showed that naphthalene, the most prevalent binuclear aromatic compound in most hydrocarbon sources, can be hydrogenated at room temperature and atmospheric pressure when rhodium is used as the catalyst. In some of the hydrogenations tetralin was the major product.

In contrast to hydrogen gas, formic acid is also used in absence of catalysts for the hydrogneation of adducts formed from ketones and amines (24) and in the hydrogenolysis of certain alcohols, such as triphenylcarbinol (25). Moreover, decomposition products of formic acid are carbon monoxide (the anhydride of formic acid), water, hydrogen, and carbon dioxide.

These are commonly present in the liquefaction of hydrocarbon residues and could play an important role in liquefaction processes.

According to recent work (26) on the conversion of coal to liquid fuels a $CO/H_2O/KOH$ system at 400°C affords products, which are quite similar to those obtained when tetralin is used as a hydrogen donor and the conditions are kept otherwise identical. As with basic systems employing methanol and isopropanol instead of carbon monoxide and water, significant reductions in organic sulfur levels were found. Using anthracene as a model compound the $CO/H_2O/KOH$ and the basic alcoholic system afforded the 9,10-dihydro-analog. It was proposed that the above systems and tetralin reduce polynuclear aromatic compounds in coal by hydride transfer rather than by the "capping" of carbon radicals with hydrogen atoms. In the $CO/H_2O/KOH$ system the formate anion, $HCO_2^-$ was considered to be the hydride donor.

In the Oxo-reaction, which is effected by a Fischer-Tropsch catalyst(27) hydrogen and carbon monoxide add to olefinic double bonds. A $CH_2OH$ is added to one of the carbon atoms of the latter while the other receives a hydrogen atom. Under the conditions of the Oxo-reaction certain olefins are also hydrogenerated, i.e. incorporate only hydrogen. It has been reported, that in such hydrogenations the catalyst is much less readily poisoned by sulfur containing compounds than hydrogenations which are identical except that carbon monoxide has been left out(28)

# EXPERIMENTAL

## Formic Acid Hydrogenation Apparatus

The hydrogenations were performed in round bottom flasks having long necks and a B-14 socket and stopper. During the preparation of the mixtures the individual ingredients were added against a stream of nitrogen. To facilitate this and to ensure that absence of atmospheric oxygen the empty flasks were first flashed well with purified nitrogen. The atmosphere of nitrogen was maintained by a tube with a side arm. The B-14 cone of the tube rested in the B-14 socket if the flask. A funnel was inserted into the tube, the lower tip of which was well below the side-arm and the ingredients were then added through the funnel. Blowing out of material, especially of the fluffy, light catalyst by nitrogen, was thus prevented (see figure 26). The flasks and the tube with the side-arm were made by a local University-employed glass-blower.

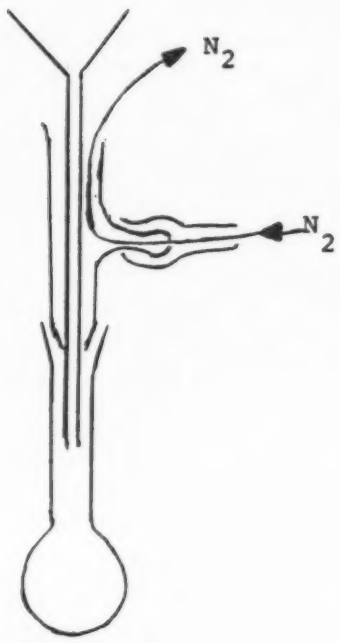
The tubes with the side-arm were replaced by a well fitting B-14 hollow glass stopper. The filled flasks were then shaken in a reciprocating shaker (see fig. 27) owing to their long necks, no catalyst or liquid reached the stopper during the shaking. Sample were taken against a stream of nitrogen and filtered through a plug of "Kim-Wipe", which closed the lower end of a Pasteur pipette and had been washed with the solvent used in the hydrogenation.

## Development of Analytical Procedure

It appeared useful to rely initially on thin layer chromatography and qualitative uv-spectroscopy,

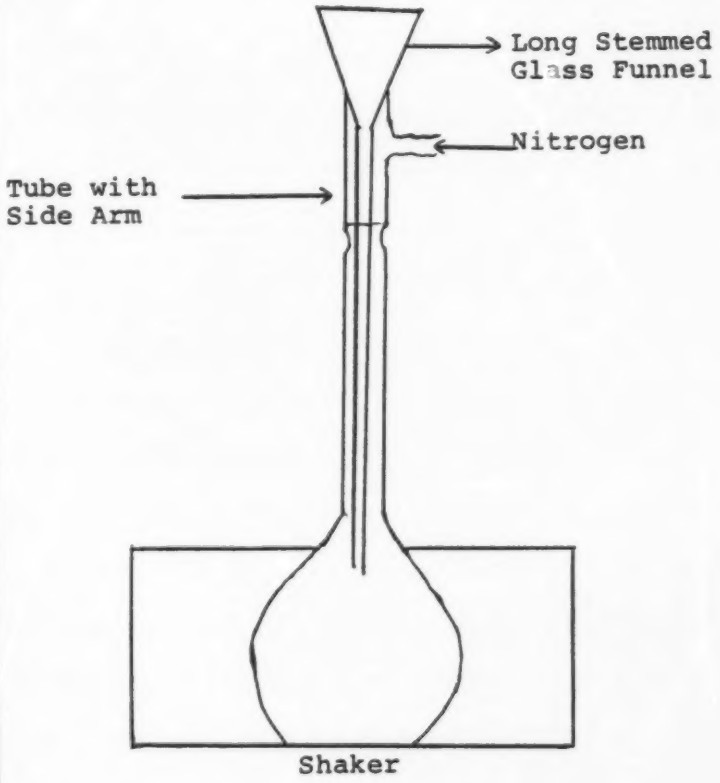
Formic Acid Hydrogenation Apparatus

Figure 26



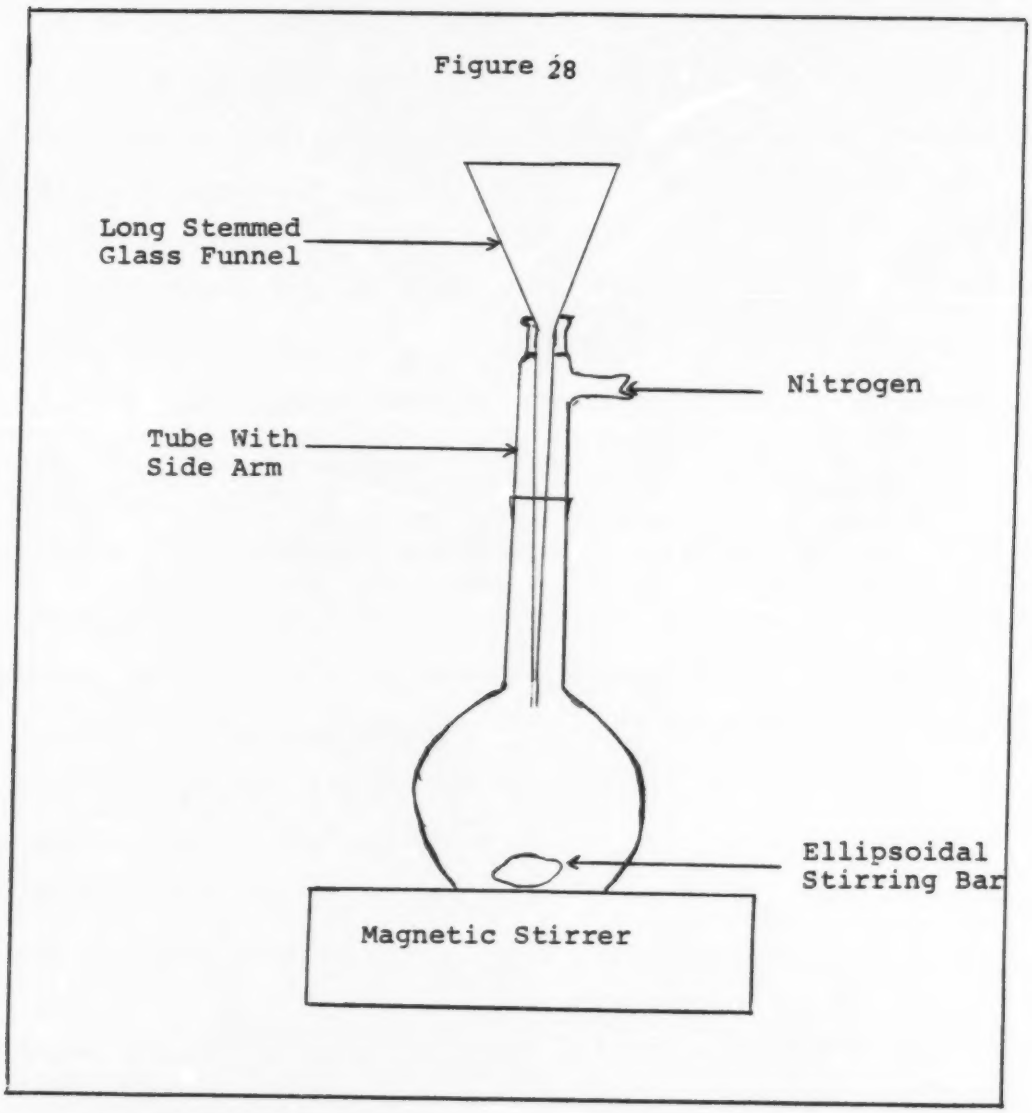
Formic Acid Hydrogenation Apparatus

Figure 27



Formic Acid Hydrogenation Apparatus

Figure 28



which allow the convenient monitoring of chemical transformations of organic compounds.

In the formic acid hydrogenation TLC and UV Spectroscopy proved useful in showing that essentially no uptake of hydrogen took place under the conditions chosen. It was planned that once broad trends of reactivity have become apparent, the methods will be substituted by methods more suitable for an accurate quantitation of the products produced, in particular by gas chromatography and elemental analysis. In the work on formic acid hydrogenations elemental analysis showed that the starting material contained sulfur, which could have inhibited the attempted reactions.

For analysis of the samples of the formic acid hydrogenations the filtered samples were spotted on alumina coated, aluminun backed fluorescent thin layer plates. The starting meterial (phenanthrene) and 9,10--dihydropehanthrene, were spotted as references. Heptane was used as the developing solvent in most chromatographies. Visualisation was carried by illumination with short and long wave uv-light and by spraying with sulfuric acid and subsequent heating. Also a part of the samples was dried and its uv-spectrum was established. Initially the analysis by thin layer chromatography was carried out on silica gel G coated alumina and glass plates. In contrast to the alumina plates, where phenanthrene and its 9, 10-dihydro space analog showed a difference in rf-valves satisfactory for analytical purposes, only a barely discernible separation of the two compounds appeared realizable on silica gel G coated plates, which are generally preferred over alumina coated plates.

Effect of Poisons on Formic Acid Hydrogenation

Commercial phenanthrene, 98%, from Aldrich Chemical Co., was used. The 9, 10-dihydro analog, which was used as a reference compound, was also obtained from the latter company. Thin layer chromatography indicated that it contained additionally some less polar material, which was considered to have arisen from the over hydrogenation of the dihydro analog.

Six hydrogenations of phenanthrene were attempted. In all of these platinum was used as the catalyst. In one of the hydrogenations hydrogen gas instead of formic acid or its anion was used.

Experiment #1

In the first reaction 88% formic acid (23 wt. %) was added dropwise with external cooling by an ice-bath to t-butylamine (36.5 wt.%). Considerable fog formation took place despite the cooling and slow addition. The phenanthrene (4 wt. %) was then added, followed by a suspension of 5% platinum on carbon (2 wt. %) in part of the heptane used. The remainder of the heptane was then added. A total of 34.5 wt % of the latter solvent was used. All additions were carried out under nitrogen, as explained above.

After shaking at room temperature for 3 days and sample taking the mixture was well immersed in a water-bath having a temperature of 60-62$^{o}$C and shaken for 3 hrs. A sample was taken and the mixture was shaken for 4 days with a volume of water, which was twice the volume of the formic acid used.

Experiment #1 Cont'd

After the water addition the mixture became more mobile but still no hydrogenation appeared to occur.

Experiment #2

The second reaction was identical to the first, except that the formic acid was added last, i.e. after the phenanthrene, platinum, heptant and t-butylamine had been added. There was less fog-formation.

Experiment #3

In the third reaction the heptane was substituted by ethyl acetate and the amount of catalyst (5% platinum on carbon) per starting material was doubled to 1 g per gram. Also the mixture was shaken intermittantly for 7 hrs. in a water-bath having a temperature between 85 and 90$^{o}$C. During the shaking and heating the glass stopper was firmly secured with rubber bands.

Experiment #4

The fourth reaction was carried out as the third except that the ethyl acetate was substituted by glacial acetic acid.

Experiment #5

The fifth reaction was carried out as the fourth reaction, except that the t-butylamine was omitted. In the fifth reaction free cormic acid rather than the t-butylammonium formate was thus present.

Experiment #6

The sixth reaction, which was considered as a reference reaction, was carried out as the fifth except that the nitrogen in the flask was replaced by hydrogen gas (more than 10 moles $H_2$ per mole phenanthrene) and that the formic acid was omitted.

The results of the experiments 1 to 6 are summarized in table 26

Table 26

Yield of Reaction Products and
Unconverted Reactants in Attempted
Hydrogenations with Formic Acid and Formate Anion

| Experiment number | Unconverted reactant | Reactant products |
|---|---|---|
| 1 | close to 100% | close to 0% |
| 2 | " | " |
| 3 | " | " |
| 4 | " | " |
| 5 | " | " |
| 6* | " | " |

*Reference reaction using hydrogen gas instead of formic acid or its anion.

## Effect of Catalysts on Formic Acid Hydrogenation

A preliminary reaction was carried out in which phenanthrene in heptane was shaken in presence of formic acid with a larger excess pf 5% rhodium on carbon. After prolonged shaking only the presence of starting material could be detected by thin layer chromatography and uv-spectroscopy.

## Effect of Reaction Variables

Initial work on the catalyst concentrations and of the ratio of formic acid-t-butylamine is discussed under the effect of poisons. This work was carried out already at an early stage in effort of forcing the transfer of hydrogen from formic acid or its anion to phenanthrene by catalysis with the platinum metal and to demonstrate the feasibility of the process.

## Discussion

The chromatograms and uv-spectra of the products of all reactions showed only phenanthrene, the starting material, even when the duration of the reaction was longer than a week and despite the heating. It was suspected that the purchased phenanthrene contained sulfur, the presence of which is not stated in the supplier's catalog. The amount of sulfur found by elemental analysis at Guelph Chemical Laboratories in two different batches received amounted to 0.44 and 0.62%. The work statement specified the addition of thiophene in an amount of 1% of the reactant (phenanthrene), which corresponds to 0.38% of sulfur.

Discussion Con't

Thus the amount of sulfur already present on the commerical phenanthrene exceeds the amount of sulfur present in the thiophene specified.

In an analysis reported in the literature phenanthrene was found to be the major component in an creosote oil and dibenzothiophene was the only identifiable sulfur containing compound. As coal tar is a source of commercial phenanthrene it may be considered that the sulfur containing impurity in the purchased phenanthrene consists essentially of dibenzothiophene. After the attempted hydrogneations the literature was consulted for methods suitable for the removal of sulfur in commercial phenanthrene. One definite method was found which appeared some-what hazardous as it involved the formation of pyrophoric soduim (29). The literature also indicated the possibility of employing other methods, such as the purification of commercial phenanthrene by preparative high pressure liquid chromatography (30, 31).

In view of the unsuccessful runs and difficulties the effect of poisons on the hydrogenation by formic acid and its anion was discontinued and efforts were concentrated on the hydrogenation of phenanthrene by flash hydropyrolysis.

Recommendations

A list of other catalysts besides platinum and rhodium i.e. Raney Ni, Raney Fe, Raney Co, were planned to be studied. These catalysts may be less readily poisoned by sulfur compounds than platinum and rhodium.

Perhaps it is useful to try the hydrogenation with formic acid and its anion after the FHP-experiments have established an order of preference among the catalysts selected. Also it may be considered to feed the flash hydropyrolysis apparatus with formic acid, a suitable formate or presursors of formic acid or formates, such as CO + $H_2O$, CO + $H_2O$ + KOH and Co + $H_2O$ + amine, respectively. Hydrogen gas, $H_2$, and carbon dioxide may be added to these mixtures in some experiments. Conceivably, in presence of formic acid, its salts and derivatives, lower temperatures may be required to effect the uptake of hydrogen than in the presence of hydrogen alone.